Petition

Distillated Tall Oil
For Addition to National List

Under the Provisions of Organic Foods Production Act

Requirement:

7 CFR 205.601
Synthetic Substances Allowed for Use inOrganic Crop Protection

DEC 15 2008

Prepared By:
Regulatory Affairs Department

Biomor Israel Ltd.
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Petitioner;
Biomor Israel Ltd.
P.O.Box 81
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Effective Organic Biocides
BIOMOR

November 30, 2008

Program Manager
Untied States Department of Agriculture
Agriculture Marketing Service /T & M
National Organic Program
1400 Independence Avenue , SW
Room 4008-S., Ag Stop 0268
Washington, D.C. 20250
U.S.A

DEC 15 2008

Subject: Petition to include Distillated Tall Oil (CAS no. 8002-26-4) on National List.
Petitioner: Biomor Israel Ltd.

Dear Sir/Madam:

We, Biomor Israel Ltd., are submitting this petition to add Distillated Tall Oil (CAS no. 8002-26-4) to National List.
Tall Oil is a by-product of the Kraft process of wood pulp manufacture and is a natural constituent of the pine tree.
In accordance with the Food Quality Protection Act, in 2006 the EPA completed reassessments of inert ingredients used in pesticide products to ensure that such products met human health based on safety standards. As a result, Tall Oil was exempt from the requirement of a tolerance under 40 CFR 180.910 by the Environmental Protection Agency for use in pesticide formulation applied to growing crops and crops after harvest (pre-and post harvest uses).

Our product 'Timorex Gold' is a biofungicide used for the control of a wide range of plant pathogens in various crops. Our product contains, in its formulation, the petitioned substance, Distillated Tall Oil (CAS no. 8002-26-4). This substance was selected as a suitable emulsifier/solvent in the formulation because of the advantage of its low toxicity to mammals and to the environment.

The petition is prepared in accordance with regulations 7 CFR 205.601 and 205.607 and also with the procedures outlined for the National List Petition Process.

Enclosed please find our petition for your review. We kindly request you to amend 7 CFR part 205 for inclusion of Tall Oil (CAC no. 8002-26-4) in the National List.

A member of the Stockton group

Biomor Israel Ltd. P.O.B 81, Qatzrin 12900 Israel • Tel. 972-4-6850525 • www.biomor.com • biomor@biomor.com

If you require further information regarding the petition, please do not hesitate to contact us.

Sincerely,

Mrs. Plia Birka & Mrs. Polli Manash
Plia Birka. Manash
Regulatory Affairs
Biomor Israel Ltd.

Cc: Mr. Dani Neifeld – COO

Introduction

Tall Oil is a by-product of the Kraft process of wood pulp manufacture and is a natural constituent of the pine tree. Tall Oil, also known as 'tallol' or 'liquid resin' , has three major components : resin acids, fatty acids and unsaponifiables .

In accordance to the Food Quality Protection Act of 2006, the EPA completed reassessments of inert ingredients used in pesticide products to ensure that such products met human health, based on safety standards. As a result, Tall Oil was exempt from the requirement of a tolerance under 40 CFR 180.910 by the Environmental Protection Agency for use in pesticide formulation applied to growing crops and crops after harvest (pre-and post harvest uses);

Biomor Israel Ltd., use Distillated Tall Oil (CAS no. 8002-26-4) in the formulation of our bio natural Plant protection product. We use this substance because of its low toxicity to mammals and environment and it was found suitable as emulsifier/solvent in our formulation.

There are several published reports on the use of our Tall Oil substance (CAS no. 8002-26-4) which includes crude and distilled Tall Oil. In the HPV publication, the Tall Oil relates to a variety of Tall Oil derivatives: Tall Oil, Tall Oil Pitch, Tall Oil Pitch sodium salt ,Tall Oil disproportionated, Tall Oil sodium salt, Tall Oil potassium salt, Tall Oil soap acidulation and wastewater. All these substances are similar in their chemical composition, being predominantly the extractives that remain after the pulping of wood.

In support of the petition, we have submitted the required information on the Tall Oil (CAS no. 8002-26-4) and the petitioned substance Distillated Tall Oil that includes the identical , physical and chemical properties, toxicity data, ecotoxicity, environmental impact, human health (safety to humans) , registrations status and other information.

PETITION FOR THE ADDITION OF TALL OIL TO 7 CFR 205.601

DEC 15 2008

ITEM A
Category for which substance is being petitioned:

Biomor Israel is petitioning for the inclusion of Distillated Tall Oil in the category of organically produced agricultural products allowed as ingredients in or on processed products labeled as "organic" under Section 7 CFR 205.601 (synthetic substance allowed for use in organic crop production).

The NOP defines as "synthetic " substance , substance that is formulated or manufactured by a chemical process or by a process that chemically changes ,a substance extracted from naturally occurring plant, animal, or mineral sources, except that such term shall not apply to substances created by naturally occurring biological processes.

The Distillated Tall Oil is one of our inert ingredients in our pesticide EC formulation used for control of pathogens for several crops.

ITEM B
1. The substance's common name.

Tall Oil.

2. The producer or manufacturer's name, address and telephone number

Forchem OY

Pal 16 (Maanpaantie 3)

FIN-26101 RAUMA,FINLAND

Tel- +358(0)2 478 4400

Fax +358(0)2 478 4499

y-tunnus 1614382-3

VAT FI16143823

3.The intended or current use of substance such as use a pesticide ,animal feed additive, processing add, nonagricultural ingredient, sanitizer or disinfectant.

Intended use of the petitioned substance as a pesticide: It is Biomor intention to use Tall Oil as one of the inert ingredient in our EC pesticide formula.

The substance functions in the pesticide formulation used as solvent/emulsifier.

The Tall Oil used in pesticide formulation by our company is a Distillated Tall Oil product (Forchem Finland Company Product).
Distilled Tall Oil is an excellent raw material to be used in metal working fluids, oil field chemicals, soaps, cleaners and alkyds resins (as remarked in Forchem Company(Finland) for utilizing Distillated Tall Oil Products **Attachment 1 and Attachment 2** Product data sheet Distillated Tall Oil For 20X,**section 3**.

Uses and application of Tall Oil other than pesticide:

- Tall Oil, also known as liquid rosin, is a resinous yellow-black oily liquid composed of a mixture of rosins, fatty acids, sterols, high-molecular alcohols, and other alkyl chain materials; obtained as a byproduct in the treatment of pine pulp.

- The crude Tall Oil is distilled into Tall Oil rosin (having the rosin content of 10 - 35%), further refinery gives to Tall Oil fatty acid (the rosin content of 1 - 10%).

- Pitch is used as a emulsifier of asphalt and as a binder of cement and adhesive. Rosin is used as a raw material for rubbers, paper size, inks, and adhesives. It is used as an emulsifier in SBR polymerization for fluidity increasing. It is used in ore flotation, corrosion inhibitors and crude dimmers applications.

- Tall Oil fatty acid (TOFA) is a low cost unsaturated fatty acid (oleic acid) and is a source of low boiling point fatty acids. It is an alternative to tall low fatty acid in soap applications. It is used as a dryer in varnishes and paints. It is used in paper sizes, inks, adhesives, alkyd resins, linoleum, oilcloth, cleaners, lubricants, dimer acids, surfactants, oil field chemicals, greases and ore flotation reagents.

- Tall Oil in used in Chemurgy branch of applied chemistry concerned with the industrial use of biomass for fuel and chemicals. The biomass may be industrial crops, such as trees, cotton, or oilseeds; food crops, such as corn or soy; or wastes and by-products, such as forest trimmings, Tall Oil, or straw.

  Attachment 3, section 3: Chemurgy Standard Article J. Peter Clark

A. Epstein and Sons International, Inc. Article Online Posting Date: December 4, 2000, cited on Kirk-Ohlmer Encyclopedia

Tall all used as a Pesticide (Plant protection product)

TALL OIL used as an insecticide:

In a study "Diterpene resin acids: major active principles in Tall Oil against variegates cutworm,, *Peridroma saucia(*Lepidoptera :Noctuidae)", Tall Oil has been shown to have insecticidal properties . This study confirms that resin acids are major active principles in Tall Oil against the variegated cutworm, but other chemicals likely also contribute to the bioactivity of Tall Oil.
In the present study, the active principles in Tall Oil against the variegated cutworm, *Peridroma saucia* ((Lepidoptera :Noctuidae)", were investigated. GC-MS analysis showed that abietic, dehydroabietic, and isopimaric acids were major resin acid components of crude Tall Oil and depitched Tall Oil.
When crude Tall Oil samples of differing resin acid composition were incorporated into artificial diet at a concentration of 2.0% fresh weight, they suppressed larval growth by 45–60% compared to controls. This suppression was significantly (P<0.05) correlated with the equivalent contents of abietic, dehydroabietic, isopimaric, and total resin acids. These results were also evident from a diet choice test, showing that the second-instar larvae obviously selected diets with low levels of resin acids when different diets were randomly arranged in a Petri dish. Bioassays with pure resin acids (abietic, dehydroabietic, and isopimaric acids) demonstrated that all individual chemicals have similar bioactivity against this insect. Comparison of the bioactivities of depitched Tall Oil and an equivalent mixture of pure resin acids in the *Peridroma* chronic growth bioassay indicated that pure resin acids and depitched Tall Oil share a common mode of action to this insect.

(**Attachment 4, section 3**: Yongshou Xie et. al., Diterpene resin acids: major active principles in Tall Oil against variegates cutworm,, *Peridroma saucia(*Lepidoptera, Noctuidae) Journal of Chemical Ecology, Vol. 19, No. 6, 1993.

Tall Oil is used as an adjuvant

CAS Number: 8002-26-4
Manufacturer: Adjuvant unlimited, inc.
Registered in : California and Philippines

(**Attachment 9, section 3:** Regulatory information for Tall Oil and Tall Oil registration status as adjuvant in PAN)

Tall Oil compound used in nonfood use pesticide products:

The following inert ingredient Tall Oil compound is permitted for use in nonfood use pesticide products:
CAS no. 100684-20-6 is contained as Inert ingredients as described in 40 CFR Part 180, EPA that may also be used in nonfood use pesticide products:

(**Attachment 7, section 3:** Inert Ingredients Permitted for Use in Nonfood Use Pesticide Products Last Updated January 7, 2008, UNITED STATES ENVIRONMENTAL PROTECTION AGENCY)

Tall Oil used as a repellent

Tall Oil (CAS no. 8002-26-4) is known to be used as a pesticide (insecticide repellent). Recently this substance was approved by EFSA (European Food Safety Authorization) and included in the EU Annex 1 inclusion of the EU registration directive, EEC 91/414.

(**Attachment 10, section 3**, Registration status of active ingredients authorized in EU, registration as a repellent)

Tall Oil used as a food additive (by FDA, USA)

- **Tall Oil rosin, glycerol ester of MISC (miscellaneous)** , REG (food additive for which a petition has been filed and a regulation issued), GMP – Title 21 CFR 172.615 Rosin, Tall Oil, glycerol ester- MISC, REG, GMP.
- **Softener for chewing gum** Title 21 CFR 172.615.
- **Chewing gum base:** glycerol ester of Tall Oil resin, etc. – Title 21 CFR 172.615.
- **Defoaming agents and components:** tallow - hydrogenated, oxidized, or sulfated; hydrogenated tallow alcohol, oleic acid from Tall Oil fatty acids – AF-Antifoaming (or defoaming) agent, REG, In foods. See individual chemicals for uses and limitations - Title 21 CFR 173.340
- **Tall Oil rosin, glycerol ester of** - MISC, REG, GMP, Softener for chewing gum - Title 21 CFR 172.615
- **Tallow alcohol, hydrogenated** – AF(, REG, GMP, Comp of defoaming agent - Title 21 CFR 173.340
- **Tallow, fatty acids** - MISC, REG, GMP, In foods - Title 21 CFR 172.860
- **Tallow, hydrogenated, oxidized or sulfated** - AF, REG, GMP, X-ref - Comp of defoaming agent - Title 21 CFR 173.340
- **Glycerol ester of Tall Oil rosin** - MISC, REG, GMP, Softener for chewing gum base (See specs in Title 21 CFR 172.615)

Definitions:

REG =food additive for which a petition has been filed and a regulation issued)

AF=Antifoaming (or defoaming) agent

MISC=Miscellaneous

(**Attachment 8, section 3**: CFSAN/Office of Food Additive Safety
July 2006, Food additive status List)

Examples from Industry:

A) Tall Oil products are intended to use for plastics, fuels and lubricants (Arizona chemical Products: Sylfat® TOFA, Sylvatal® DTO and Sylvaros®).

*An Arizona chemical company product, named Sylvatal DT-3, is a distilled Tall Oil product emulsifier for soluble oil and liquid soap for use in pine oil cleaners and other synthetic detergents.

*Arizona Chemical is the world's largest producer of naturally derived specialty resins and pine-based chemicals for the adhesives, inks and coatings, lubricants, fuel additives, mining and oleochemicals markets

Rosins are the core group of Tall Oil products that Arizona chemical Products manufacturers globally. They are used in a wide variety of applications including alkyd paints.

Attachment 5, section 3 : Arizona chemical -Product –Applications-Surfactants

B) Distilled Tall Oils used as Emulsifier in the polymerization of synthetic rubber:

Meadwestvanco Company use Tall Oil chemicals used as emulsifiers in the polymerization of synthetic rubber and extended SBR latex, metalworking oils, alkyd resins, anionic flotation reagents and asphalt emulsion additives. These products include distilled Tall Oils and stabilized mixed acids.

A Meadwestvanco Company chemical company product, named MWV M-28B is a medium-colored Tall Oil distillate and contains fatty acids and approximately 30 percent rosin. It offers improved quality in fatty acid applications where rosin content and light color are important. It is used as an emulsifier for oil extended SBR latex and for metalworking oils, as a base for alkyd resins, as an anionic flotation reagent, to formulate pine oil cleaners and as an asphalt emulsion additive).

Attachment 6, section 3: Meadwestvanco Company chemical company product, named MWV M-28B MWV , Distilled Tall Oil and Mixed Acids Specialty Chemicals pine.chemicals@mwv.com

4. A list of the crop, livestock or handling activities for which the substance will be used. If used for handling (including processing), the substance's mode of action must be described.

Our pesticide is used for control of several pathogens in agriculture food crops (Powdey mildew, Downy mildew, Alternaria, Late blight, Early blight, Black Sigatoka) in various vegetables in greenhouse and open field (tomatoes, cucurbits, potatoes , pepper , squash) plantations (Mango, Banana), ornamentals (Rose), herbs (Parsley)and orchards (vineyards, grapes).

The mode of action of Tall Oil is related to his function as solvent/emulsifier (a surface-active agent that promotes the formation of an emulsion). It stabilizes mixtures of oil and water by reducing the surface tension at the interface between the oil and water molecules. Because water and oil do not dissolve in each other a surfactant has to be added to the mixture to keep it from separating into layers. As an emulsifier, Tall Oil stabilizes the emulsion; it is a surfactant blend of "surface acting agent".
Tall Oil is an organic compound with amphiphilic, meaning they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads").

5. The source of the substance and a detailed description of its manufacturing or processing procedures from the basic component(s) to the final product.

a) Source: Tall Oil is a native rosins (i.e., gum, wood, Tall Oil, and dark wood), which are the purified and distilled rosins from the balsam of various species of pine (up to 80 (different species), each have their own extraction method.

Tall Oil, also called liquid rosin or tallol, is a viscous yellow-black odorous liquid obtained as a byproduct of the **Kraft process of wood pulp manufacture**.

Attachment 1, section 5: process, Wikipedia

The name originated as Anglicization of Swedish "tallolja" ("pine oil").

Tall Oil is a major by-product of the kraft or sulfate pulping process employed in the manufacture of paper. In such a process, rosin acids and fatty acids which occur in pine wood as free acids or their esters are saponified in the black cooking liquor to their corresponding sodium salts.

Black liquor separated from the cellulose portion of the wood in a kraft pulping process contains, among other things, sodium sulfite, sodium sulfide, about 8% sodium salts of lignin materials, fatty acid soaps, rosin acid soaps, and unsaponifiable organic compounds. The soaps which separate from the aqueous phase at a stage during evaporation of water from the black liquor float on the partially concentrated black liquor to form a layer of soap skimmings. The *recovered skimmings a*re trated as following :

1.treated with sulfuric acid to convert the soap skimmings to the free carboxylic acid form known as *crude Tall Oil*.

Crude Tall Oil is a dark brown mixture of fatty acids, rosin, and neutral materials. The fatty acids are primarily a mixture of unsaturated oleic and linoleic acids and saturated palmitic and stearic acids. Rosin is composed of resin acids. Crude Tall Oils are fractionally distilled to separate them into heads (low boiling fractions), Tall Oil fatty acids, *distilled Tall Oil (mixed fatty and resin acids),* rosins, and pitch (residue). Crude Tall Oil contains rosins, unsaponifiable sterols (5-10%), resin acids (mainly abietic acid and its isomers), fatty acids (mainly palmitic acid, oleic acid and linoleic acid), fatty alcohols, some sterols, and other alkyl hydrocarbon derivates. By fractional distillation Tall Oil rosin is obtained, with rosin content reduced to 10-35%.

The Tall Oil fractionally distilled product collected from the mid-cut fractions of the crude Tall Oil, i.e., the Tall Oil fatty acids, distilled Tall Oil, and rosins, are widely employed as emulsifiers (Example :in polymerization of rubber).

2.In addition, the soap skimmings carry with them some black liquor, as a result of incomplete separation, and this black liquor contains lignin salt a lower molecular weight fraction of which, after acidification, will dissolve in the crude Tall Oil acids. Thus, black liquor left in the soap contributes to the lowering of the crude Tall Oil quality and its acid number. *Acid number* is a measure of the free resin acids and fatty acids available and recoverable, and expressed in the number of milligrams of KOH per gram of sample needed to neutralize the same.

Description of products Tall Oil obtained by Forchem and used in the Biomor pesticide product:

Tall Oil products are natural raw materials for many industrial processes which serve us in a variety of ways. They are used, for example, in paints and coatings, coating additives, surfactants, metalworking, oilfield chemicals, oil and fuel additives, pulp and paper chemicals, printing inks, adhesives or bio fuels.

The main Forchem 's product groups ,distilled from the crude Tall Oil are: Tall Oil fatty acid (TOFA), distilled Tall Oil (DTO), Tall Oil rosin (TOR) and heads Tall Oil pitch. **Attachment 2, section 5:** Tall Oil Life Cycle (Forchem)

Attachment 3, section 5: Fractionation of the Tall Oil (Forchem)-for crude Tall Oil

Attachment 4, section 5: Fractionation of Crude Tall Oil (Forchem)-description letter provided by Quality Manager of Forchem Tall Oil Refinery in Rauma, Finland.

In our product the distilled Tall Oil (DTO) is used as an inert component.

b) Manufacturing and Processing:
Full description is provided by Forchem company in the following documents:
Attachment 6, section 5: Full Tall Oil scheme of the technological process (manufacturing process in Finnish);

Attachment 5, section 5: Production chain Forchem for crude Tall Oil;

Attachment 3, section 5: Fractionation of the Tall Oil (Forchem)-for crude Tall Oil;

Supporting attachment data: **Attachment 7, section 5:** Figure 1-Tall Oil Process Forestry Tall Oil

Tall Oil is a mixture of mainly acidic compounds found, like turpentine, in pine trees and obtained as a by-product of the pulp and paper industry.
It is extracted at the pulp and paper mill, and undergoes the first two processing steps.
General description information of the full process including the following steps:

Step 1 - Extraction of Tall Oil soap

The "black liquor" from the paper making process is concentrated and left to settle.
The top layer is known as "Tall Oil soap", and is skimmed off.
The rest is recycled for further use in paper making.

Step2 - Production of crude Tall Oil

The Tall Oil soap is reacted with acid to form crude Tall Oil. The following reaction occurs:

R—COONa + H3O+ → R—COOH + H2O + Na+

The acids formed from this reaction, along with small quantities of other compounds of similar volatility, make up the crude Tall Oil.

Factors affecting quality of CTO are as following:

A. Wood type has an influence on the quality of Tall Oil, different woods produce different proportions of resin acids, fatty acids and unsaponifiables, and different total amount of oil. In general, older and slower growing trees produce more resin acids (since they have more heartwood).

B. The condition under which the acidification is carried out has a bearing on the quality of the oil. Acid number (a measure of the quantity of resin and fatty acids in the oil) may drop duet decarboxylation or esterifcation, both of which are favoured by the presence of strong acid.

Using H2SO4 as the acidifying agent lowers the quality of the oil.

Polymerisation, which only reduces the acid number when it occurs through the carboxylate groups, is also favoured by concentrated sulphuric acid. This in itself does not reduce acid number (unless polymerisation is carried out through the carboxylate group as in proteins), but does make the oil more viscous and increases the proportion of oil in the lignin emulsion.

The only practical alternative would be boric acid (B (OH)3), which is a suitable weaker acid, but it is expensive and interferes with the paper making process. For this reason H2SO4 is still used. In default of a suitably cheap and practical weak acid, it has been found that dilution of the soap, before acidification, in the ratio of 8 parts soap to 1 part water, produces significant yield improvement and requires less mixing and less acid to reach the desired pH.

C. The oil storage time and temperature have an influence on the quality of the Tall Oil.

Temperatures above 60°C favor the formation of esters between the acids and the various alcohols (sterols, higher alcohols) present in the unsaponifiable part of the oil. The longer the oil is left, the further this esterification proceeds.

Step 3 - Crude Tall Oil distillation

The oil is distilled into five components with different boiling points: heads (which boils first), then fatty acids, distilled Tall Oil (a mixture of fatty and resin acids), resin acids (collectively known as rosin) and pitch (the residue). All of these can be used in various industries as is, but some of the rosin is also further processed on site.

The crude Tall Oil is a mixture of fatty acids and resin acids along with various other materials such as unsaponifiables. The fatty acids are generally more volatile than the resin acids and hence these two products can be separated to a large degree by distillation. The impurities also have volatility differences so that they too can be distilled off first (the light ends) or left behind as residues at the end of distillation. There are, however, some overlaps in volatility so that perfect separation is not possible. The heavier fatty acids and the lighter resin acids cannot be separated by distillation alone and hence there is an intermediate distillation cut called DTO (distilled Tall Oil) which consists of about 30% resin acids, 65% fatty acids and perhaps 5% of other substances. A distillation of CTO therefore yields effectively five streams or cuts. For typical Forchem Tall Oil Rafinery Finland, fractionation distillation can be divided in 7 main stages:

1) Dehydration of CTO
2) Pitch separation from CTO;
3) Rosin separation from CTO;
4) Heads separation from CTO;
5) Fatty separation from CTO;
6) Distillated Tall Oil separation;
7) Heavy fraction separation and utilization for energy.

Separation of different fractions is based on their different physical properties and all the parameters are considered by the manufacturer as confidential.

Attachment 4, section 5: Fractionation of Crude Tall Oil (Forchem)-description letter provided by Quality Manager of Forchem Tall Oil Refinery in Rauma, Finland

The distillation is carried out as a continuous operation comprising the following the following separation stages:

Dehydration
Removal of water and volatiles from the crude Tall Oil feedstock yielding a heads stream.

Depitching
Removal of nonvolatile materials from the crude Tall Oil to provide a residue stream and to minimize operating problems in subsequent stages.

Rosin separation
Recovery of rosin as the bottoms product in the first distillation column which is about 40 m tall by 1.5 m diameter.

Heads separation
Removal of impurities (heads) from the overheads coming from the rosin column prior to recovering the fatty acids. These heads are the top product from the second distillation column of about 30 m tall by 0.6 m diameter.

Fatty acid separation
Recovery of high grade fatty acids as top product and distilled Tall Oil as bottoms in the last distillation column. Each column has a feed and top and bottom offtakes, providing two fractions from each stage of the distillation process. The higher volatility materials will go to the top and fractioning the lower volatility substances to the bottom. One fraction from each stage provides the feed to the next stage whilst the other fraction yields either a product or a recycle or residue stream.
Heat is provided to the columns using hot oil .The columns are operated under partial reflux to increase the driving force for separation and there is also provision for recycling material from later stages back to earlier units to attain a more precise distillation cut.
The major processing feature of the distillation is that the Tall Oil and its products are very sensitive to heat. Excessive temperature or holding at temperature for long periods of time is countered by the use of very high vacuum for all the distillation columns. This measure minimizes the operating temperatures experienced by the fluids and the time to which they are exposed to heat. The high vacuum operation also helps in the distillation by exaggerating the relative volatility differences between the components, whilst also minimizing the thermal energy requirements of the process.
The net result of the distillation process is the production of three main products: fatty acids, DTO and rosin, plus some quantities of residue (pitch) and a Heads stream.
There is a reasonable market for the fatty acids and DTO, but a poor market for rosin.
The main value of rosin is that it can be used to manufacture rosin size and a variety

of other specialty substances such as rosin oils. In preparation of those rosin based products, proportions of DTO, pitch and heads can also be utilized to maximize the saleable product recovered from the CTO. Any pitch and heads which cannot be incorporated into saleable products can be used as a fuel in the Tall Oil plant itself.

Step 4 - Production of rosin paper size
"Paper size" is the substance that stops all paper from behaving like blotting paper. It is produced by reacting rosin with maleic or fumaric acid and then KOH, and mixing the resulting compound with water.
"Paper size" is a material applied to paper to make the surface less absorbent to ink.

All stages of the process are monitored by the laboratory to ensure quality is consistent. Various measures are also in place to ensure safety, as Tall Oil is highly flammable (and in its soap form is slippery as well).

The laboratory is involved exclusively in quality control. The results obtained are described in section 9 (see **attachment 1, section 9** product Data sheet).
The quality of the Tall Oil is monitored by using the acid number. This is a measure of the total acid (i.e. fatty and resin acids, so long as there is no excess of sulphuric acid) content of the crude Tall Oil.
It is determined by ordinary titration with KOH, and is expressed as mg KOH/g sample. This is a sufficiently good measure of the quality of the oil for those at Kinleith (New Zeeland), but the users of the oil have more sophisticated procedures.
The non-saponifiables are obtained from aqueous solution of the saponifiables by solvent extraction. The acids are analyzed for by acidification of the solution, causing the acids to precipitate, followed by solvent extraction and then quantitative gas chromatographic analysis.

Remark: Accurate information and description and all the parameters in Forchem process are considered as confidential.

6. The intended or current use of substance A summary of any available previous reviews by State or private certification programs or other organizations of the petitioned substance.

The petitioned substance is review by the following:

EPA Registration Number –California
Applicant / Brand Name

223880 - (1051156 - 50001)
ADJUVANTS UNLIMITED, INC.
USE: Adjuvant – for use as an adjuvant

TYPE: California only registration
CAS NUMBER(S): 61791-12-6, 61791-07-9, 61791-23-9, **8002-26-4**

Attachment 9, section 3. Regulatory information for Tall Oil and Tall Oil registration status as adjuvant in PAN .

CASRN 8002-26-4 is listed as an inert substance of unknown toxicity (list 3) under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).

CASRN 8002-26-4 is used as a feedstock to the fractionation process and separated into rosin, fatty acids, distilled CASRN 8002-26-4, heads, pitch, etc.

8002-26-4 lists uses as the manufacturing of soap pastes, flotation agents, greases, paint, rubber formulation, cutting oils and sulfonated oils.

(**Attachment 1, section 7:** Initial Risk-Based Prioritization of High Production Volume Chemicals, September 2008)
(Attachment 4, section 7, list 3 of inert ingredients in the EPA)

Tall Oil is an inert ingredient included in CFR title 40: Protection of Environment list of exception from the requirement of a tolerance. Residue of the following material is exempted from the requirement of a tolerance when use as in accordance with good agricultural practice as inert ingredient in pesticide formulation:
Tall Oil; fatty acids not less than 58%, rosin acids not more than 44%, unsaponifiables not more than 8% ,uses as surfactant, related adjuvants of surfactants.

(**Attachment 2 section 7**: e-CFR Title 40: Protection from the Environment, exemptions from tolerances, 2.10.2008)

Tall Oil (CAS no. 8002-26-4) is known to be used as a pesticide (insecticide repellent). Recently this substance was approved by EFSA (European Food Safety Authorization) and included in the EU Annex 1 inclusion of the EU registration directive, EEC 91/414.

(**Attachment 6, section 7**: Europe, existing active substances; SANCO DOC 3010)

7. Information regarding EPA, FDA, and State regulatory authority registrations, including registration numbers.

EPA

CASRN 8002-26-4 is listed as an inert substance of unknown toxicity (list 3) under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).
Non-confidential information in the US EPA, IUR indicates that there are 45 manufacturers of crude CASRN 8002-26-4, all of which are paper manufacturers, and fractionators of CAS RN 8002-26-4.
Most companies and sites use the fractionated product(s) as a reactant or component in formulated products. Non-confidential IUR information indicates a variety of uses for these chemicals including uses as intermediates, flotation agents, fuels, and adhesive and binding agents. All six chemicals have IUR submissions that indicate commercial or consumer uses. Information submitted as part of the HPV Challenge Program also provides information on uses.

CASRN 8002-26-4 is used as a feedstock to the fractionation process and separated into rosin, fatty acids, distilled CASRN 8002-26-4, heads, pitch, etc.
CASRN 65997-01-5 is used in the production of adhesives and binding agents, flotation agents, pigments, metalworking fluids and lubricants, and soaps and detergents.
CASRN 68140-16-9 is used in the asphalt industry as a bonding agent in paving applications or as a plasticizer in asphalt coatings.

CASRN 68152-92-1 is used in the production of rubber and neoprene.

CASRN 68647-71-2 is used in the production of soaps and detergents, metal-working fluids and lubricants.
CASRN 8016-81-7 is used as a fuel by the CASRN 8002-26-4 processor, and in adhesives.
8002-26-4 lists uses as the manufacturing of soap pastes, flotation agents, greases, paint, rubber formulation, cutting oils and sulfonated oils.

(**Attachment 1, section 7:** Initial Risk-Based Prioritization of High Production Volume Chemicals, September 2008)
(Attachment 4, section 7, list 3 of inert ingredients in the EPA)

Re assessment for Tall Oil by the EPA:

Tall Oil is in the re assessment process of the EPA inert list.
Tall Oil is an inert ingredient included in CFR title 40: Protection of Environment list of exception from the requirement of a tolerance. Residue of the following material is exempted from the requirement of a tolerance when use as in accordance with good agricultural practice as inert ingredient in pesticide formulation:
Tall Oil; fatty acids not less than 58%, rosin acids not more than 44%, unsaponifiables not more than 8% ,uses as surfactant , related adjuvants of surfactants.

The chemical Tall Oil (CAS# 8002-26-4) is cleared for use in pesticide products: All products applied to non-food use sites (e.g., turf, ornamental plants, highway right of ways, etc.).
For use as a surfactant in all products applied to growing crops and raw agricultural commodities after harvest under 40 CFR 180.910 and products applied to animals used for food under 40 CFR 180.930. In both sections of the CFR the name of the tolerance exemption is "Tall Oil; fatty acids not less than 58%, rosin acids not more than 44%,unsaponifiables not more than 8%".

(**Attachment 2 section 7**: e-CFR Title 40: Protection from the Environment, exemptions from tolerances, 2.10.2008)

Other derivates from or closely related to Tall Oil are also mentioned as supporting data. Methyl esters of tall-oil fatty acids are proposed to be exempted from the requirement of a tolerance when used as an inert ingredient (adjuvant) in pesticide formulations. This proposed regulation was requested by Union Camp Corporation pursuant to the Federal Food, Drug, and Cosmetic Act (FFDCA)

The Agency has decided that no data, in addition to that described below, for methyl esters of tall-oil fatty acids will need to be submitted. The rationale for this decision is described below:
(1) Tall-oil fatty acids are exempted from the requirement of a tolerance under 40 CFR 180.1001(c) as ``Tall-oil; fatty acids not less than 58 percent, rosin acids not more than 44 percent, unsaponifiables not more than 8 percent."

(**Attachment 3 section 7:** Methyl Esters of Tall-Oil Fatty Acids; Tolerance Exemption EPA 40 CFR Part 180)

FDA

Tall Oil phytosterols been proposed as generally Recognized as Safe GRAS (Notice No. GRN 000039 informs FDA of the view of Novartis Consumer Health, Inc. (Novartis).Tall Oil phytosterols, are proposed for use as a nutrient in vegetable oil spread to reduce the absorption of cholesterol from the gastrointestinal tract at a level up to 12% free phytosterols. The agency has no questions regarding the Novartis' conclusion that Tall Oil phytosterols are GRAS under condition to use and continuing responsibility of Novartis to insure that firm markers are safe.
(Attachment 7, section 7, Agency Response letter GRAS Notice No GRN 00039 and **Attachment 8, section 7**, Application A417-Tall Oil non-esterified phytosterols derived from Tall Oil, Full assessment, 10 october 2001)

The Tall Oil rosin, glycerol ester of –MISC, REG,GMP , softener for chewing gum-172.615.
Tall Oil, glycerol ester –MISC, REG, GMP.

(**Attachment 5, section 7**: Food additive status list)

EU

Tall Oil (CAS no. 8002-26-4) is known to be used as a pesticide (insecticide repellent). Recently this substance was approved by EFSA (European Food Safety Authorization) and included in the EU Annex 1 inclusion of the EU registration directive, EEC 91/414.

(**Attachment 6, section 7**: Europe, existing active substances; SANCO DOC 3010)

Registrations for other products related to Tall Oil:

Tall Oil Rosin CAS no. 8052-10-6 – Permitted in **Canada** as an inert ingredient and as a food additive.

***Tall Oil Fatty acid (fatty acid/potassium salt*) CAS no. 61790-12-3** - Registered in USA and Canada as an inert ingredient.

Sodium Tall Oil soap – Registered by the Food and Drugs Act (F&DA)in Canada, 2001.

Distillated Tall Oil fatty acids (and) potassium salt - Registered by the Food and Drugs Act (F&DA)in Canada, 2001.

Attachment 9, section 7 includes the following references:

- Substances in Cosmetics and Personal Care Products regulated under the Food and Drugs Act (F& DA) .
- PMRA Consolidated list formulants sorted by CAS Number.
- U.S. Environmental Protection Agency, List of inert Pesticide Ingredients.
- PAN Pesticide Database – Pesticide Registration Status

8. The Chemical Abstract Service (CAS) number or other product numbers of the substance and labels of products that contain the petitioned substance.

Abbreviations of basic Tall Oil names and common analyses are often used in publications and reports.
Crude Tall Oil (CTO) [*8002-26-4*]
Tall Oil fatty acids (TOFA) [*61790-12-3*]
Tall Oil rosin (TOR) [*8052-10-6*]
Distilled Tall Oil (DTO) [*8002-26-4*]
Tall Oil pitch (TOP) [*8016-81-7*]
Heads, light ends (H) [*65997-03-7*]

Category chemical CAS (CAS 8002-26-4), a by-product from the pulping of pine trees, are substances derived from or closely related to Tall Oil.
Tall Oil and derivates are complex mixtures and therefore considered by US EPA class 2 substances, composed of numerous chemicals. The most common of these chemicals are rosin and fatty acids, with lesser amounts of terpene and sterols.
All the members of this category are similar in chemical composition.

(**Attachment 1, section 8:** High Production Information System (HPVIS), information about reference Final Submission Information for Tall Oil and Related Substances Zinkel, D.F. and Russell, J., Eds. 1989. Naval Stores Production, Chemistry, Utilization. Pulp Chemicals Association, New York.).

Tall Oil and related substances (substances derived from or closely to Tall Oil) is the subject of test plan submitted to USA EPA by Pine Chemical Association
The following chemical CAS are included in the test study:
8002-26-4, Tall Oil
8016-81-7, Tall Oil Pitch
68140-16-9, Tall Oil Pitch, sodium salt
68152-92-1, Tall Oil, disproportionated
65997-01-5, Tall Oil, sodium salt
68647-71-2, Tall Oil, potassium salt
65997-02-6, Wastewater, Tall Oil soap acidulation

All these substances are composed of numerous chemicals of which are rosin and fatty acid, with lesser amounts of Tall Oil and sterols, the Tall Oil in each one containing Tall Oil, however all members of these substances are similar in chemical composition, being predominantly the extractives that remain after the pulping of wood. All are closely related to Tall Oil.

CAS No. 8002-26-4, Tall Oil (crude Tall Oil) results by acidulating Tall Oil soap with sulfuric acid.
A by-product of this acidulation is "wastewater, Tall Oil soap acidulation" (CAS# 65997-02-6), which is essentially a solution of sodium sulfate containing dilute amounts of Tall Oil. Commercially, crude Tall Oil is fractionally distilled to manufacture all oil fatty acids and Tall Oil rosin.

(**Attachment 3, section 8**: Pine Chemical Association, Atlanta: High Production Volume Chemical Challenge Program, Test Plan for Tall Oil and Related Substances, Submitted to US EPA, 2001)

Our petitioned substance is Distillated Tall Oil FC20X (CAS 8002-26-4), (manufactured by Forchem) and it is used as solvent /emulsifier in Biomor product (as Timorex Gold; their active ingredient is a natural plant extract and all its formulation ingredients are in line with the Organic Bodies requirements).

Our product is a natural bio organic fungicide.

Label of Timorex Gold is enclosed.

(**Attachment 2 :** Sample label of Timorex Gold**)**

Non-confidential information in the IUR indicates that there are 45 manufacturers of crude CASRN 8002-26-4, all of which are paper manufacturers, and fractionators of CASRN 8002-26-4.
Most companies and sites use the fractionated product(s) as a reactant or component in formulated products. There may be other companies and sites that are claimed confidential. Six of the eight chemicals in this category have IUR (Inventory Update Reporting) submissions.
Non-confidential IUR information indicates a variety of uses for these chemicals including uses as intermediates, flotation agents, fuels, and adhesive and binding agents. All six chemicals have IUR submissions that indicate commercial or consumer uses. Information submitted as part of the HPV Challenge Program also provides information on uses.
CASRN 8002-26-4 is used as a feedstock to the fractionation process and separated into rosin, fatty acids, distilled CASRN 8002-26-4, heads, pitch, etc.
CASRN 65997-01-5 is used in the production of adhesives and binding agents, flotation agents, pigments, metalworking fluids and lubricants, and soaps and detergents.
CASRN 65997-02-6, composed of dilute CASRN 8002-26-4, has no commercial value and is either recycled to the pulping process or diverted to wastewater treatment.
CASRN 68140-16-9 is used in the asphalt industry as a bonding agent in paving applications or as a plasticizer in asphalt coatings.
CASRN 68152-92-1 is used in the production of rubber and neoprene.
CASRN 68647-71-2 is used in the production of soaps and detergents, metal-working fluids and lubricants.
CASRN 8016-81-7 is used as a fuel by the CASRN 8002-26-4 processor, and in adhesives.
The Hazardous Substances U.S. Environmental Protection Agency September 2008 Risk -Based Prioritization Document 3 Data Bank (HSDB) information for CASRN 8002-26-4 lists uses as the manufacturing of soap pastes, flotation agents, greases, paint, rubber formulation, cutting oils and sulfonated oils.

(Attachment 1, section 7: Initial Risk-Based Prioritization of High Production Volume Chemicals, September 2008)

<u>Other companies manufacturing and producing TALL OIL and their Application product</u>

I. Product containing Tall Oil (CAS 8002-26-4) named ACINTOL C

Synonyms: 62046-51-9, 8002-26-4, 8032-00-6, Acintol C, Acintol D 29 LR, EINECS 232-304-6, HSDB 5049, Lignin liquor, Liquid rosin, Rosin, liquid, TALL OIL, Tall Oil (crude and distilled), Tall Oil rosin, Tall Oil rosin and fatty acids, Tall Oil [Oil, misc.], Talleol, Tallol, Unitol CX, Unitol DT 40, Yatall MA

This is a high volume chemical_with production exceeding 1 million pounds annually in the U.S. used in as flotation agents, softeners, wood stains and Varnishes in the industry of Collectors - Nonsulfide Ores, Plasticizers - Animal/Veg. Fats,Oils,Resins and drying oils.

II. MRCO Company:

Product of MRCO's company:

SYLFAT: a Tall Oil fatty acid (TOFA) with high fatty acid content and a low content of resin acids and unsaponifiables. Sylfat provides a combination of light colour, very good colour stability and air drying properties.
Sylfat applications:these products have a partially unsaturated C18 backbone and are used in wide range of applications including alkyd resins, dimer acids, surfactants, cleaners, oil field chemicals, lubricant esters and other chemical derivatives.

SYKVATAL: products are distilled Tall Oils (DTO), with 10-30% resin acids. They combine the advantages of fatty- and resin acids and are therefore and ideal raw material for functional products like metalworking flids, oil field chemicals, soaps, cleaners and alkyd resins. Vamishes for indoor use based on DTO use have hard films, with high gloss and excellent water and alkali resistance. Magnesium soaps of DTO are very efficient dispersants for fuel oils.

III.Atlanta Company:

Products of Atlanta's Company:Sylfat® TOFA, Sylvatal® DTO and Sylvaros®

Rosin is the core groups of Tall Oil products those AZC manufacturers globally. They are used in a wide variety of applications including alkyd paints.

Sylvatal ® 20S, a plant specific distilled Tall Oil (DTO), combines the advantages of fatty and rosin acids. It is therefore a suitable raw material for metal working fluids, oil field chemicals, soaps, cleaners and alkyd resins. Available in EU only.

Sylvatal 25/30L is a special distilled Tall Oil (DTO), combines the advantages of fatty and rosin acids. It is therefore a suitable raw material for metal working fluids, oil field chemicals, soaps, cleaners and alkyd resins. Available in EU only.

Sylvatal DT-30 is a distilled Tall Oil product with a rosin acid content of 30 to 35%. Its uses are in alkyd resins and Tall Oil esters for paint vehicles, emulsifiers for soluble oils and in liquid soaps for use in pine oil cleaners and other synthetic detergents

Sylvatal ® 25/30S, a plant specific distilled Tall Oil (DTO), combines the advantages of fatty and rosin acids. It is therefore a suitable raw material for metal working fluids, oil field chemicals, soaps, cleaners and alkyd resins. Available in EU only.

Sylvatal PDT An economical grade of distilled Tall Oil. This product finds applications in alkyd resins, low cost wetting agents, emulsifiers, anionic emulsifiers for ore flotation reagents.

IV. Christeyns in Bradford, West Yorkshire, UK (United Kingdom)

Christeyns (UK) Limited, part of the Christeyns Group, based in Belgium, and supplier of industrial detergents, industrial soaps and oleochemicals , concrete additives

V. Prado, Technical in Tampa, FL, US (United States)

Prado, Technical in Tampa, FL, US (United States) - Acids, Chemicals, Fine Chemicals, Specialty Chemicals, Fatty Acids (67254-79-9), Tall Oil Fatty Acids (61790-12-3), Tall Oil (8002-26-4),

VI. Distilled Tall Oil and Mixed Acids- Meandwestvaco Company

MWV Meandwestvaco Company produces Tall Oil chemicals are used as emulsifiers in the polymerization of synthetic rubber and extended SBR latex, metalworking oils, alkyd resins, anionic flotation reagents and asphalt emulsion additives. These products include distilled Tall Oils and stabilized mixed acids.

Product Options includes Distillated Tall Oils

-MWV M-15
This medium-colored Tall Oil distillate, which contains fatty acids and approximately 15 percent rosin, is used in metalworking compounds, alkyd resins and pine oil cleaners.

-MWV M-28B
This medium-colored Tall Oil distillate contains fatty acids and approximately 30 percent rosin. It offers improved quality in fatty acid applications where rosin content and light color are important. It is used as an emulsifier for oil extended SBR latex and for metalworking oils, as a base for alkyd resins, as an anionic flotation reagent, to formulate pine oil cleaners and as an asphalt emulsion additive.

-MWV M-38
This medium-colored Tall Oil distillate, which contains fatty acids and approximately 40 percent rosin, is used in metalworking formulations and in other applications requiring a high rosin content mixed acid.

Product Options includes stabilized Mixed Acids

-MWV M-30D, MWV M-40, MWV M-70
These products are blends of catalytically stabilized Tall Oil rosin and fatty acids. They are used primarily as emulsifiers in the polymerization of styrene and butadiene for synthetic rubber and in other applications requiring a blend of catalytically stabilized fatty acids and rosin acids.

M-30 contains approximately 30 percent stabilized rosin; M-40 contains 40 percent stabilized rosin; M-70 contains 70 percent stabilized rosin.

9. The substance's physical properties and chemical mode of action, including:

a. Chemistry

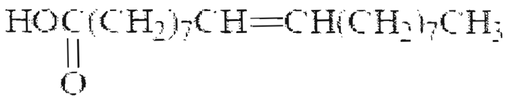
Table of content of Chemistry:

I. Composition Tall Oil-general description

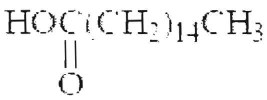
Tall Oil, also known as 'tallol' or 'liquid resin', has three major components: resin acids, fatty acids and unsaponifiables (also known as "neutral compounds"). A typical composition of Tall Oil from the Forchem is 75% free fatty acids, 20%free rosin acid and 3% unsaponifiables.
(**Attachment 1, section 9** Forchem Product data sheet)

Fatty acids

These are the long chain monocarboxylic acids which make up fats and oils and are found in both hardwoods and softwoods. The main fatty acids in Tall Oil are oleic, linoleic and palmitic acids.

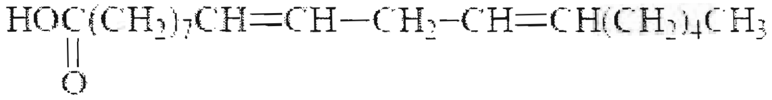


$HO\underset{\underset{O}{\|}}{C}(CH_2)_7CH{=}CH(CH_2)_7CH_3$



$HO\underset{\underset{O}{\|}}{C}(CH_2)_{14}CH_3$

oleic acid **palmatic**



$HO\underset{\underset{O}{\|}}{C}(CH_2)_7CH{=}CH{-}CH_2{-}CH{=}CH(CH_2)_4CH_3$

linoleic acid

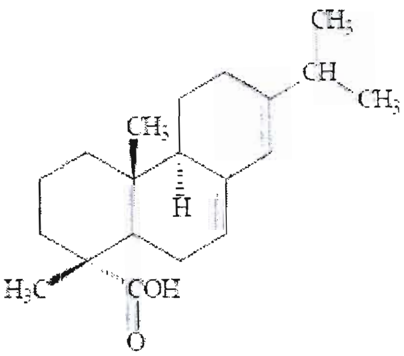
Oleic acid is a monounsaturated omega-9 fatty acid found in various animal and vegetable sources. It has the formula $C_{18}H_{34}O_2$ (or CH_3 $(CH_2)_7CH{=}CH$ $(CH_2)_7COOH$).

The saturated form of this acid is stearic acid.
Linoleic acid is an unsaturated omega-6 fatty acid. It is a colorless liquid.
In physiological literature, it is called 18:2(n-6). Chemically, linoleic acid is a carboxylic acid with an 18-carbon chain and two *cis* double bonds; the first double bond is located at the sixth carbon from the omega end. Molecular formula: $C_{18}H_{32}O_2$
Palmitic acid is one of the most common saturated fatty acids found in animals and plants. Molecular formula: $C_{16}H_{32}O_2$.

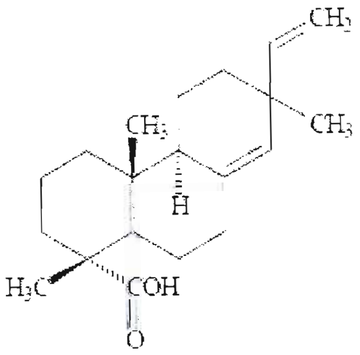
Resin acids
Resin acids are a mixture of organic acids derived from oxidation and polymerization reactions of terpenes that are found in softwoods, hardwoods and conifers. The main resin acid in Tall Oil is abietic acid, but abietic acid derivatives and other acids such aspimaric acid are also found in noticeable quantities.

Abietic acid is a resin acid, , isolated from rosin (via isomerization) and is the most abundant of several closely related organic acids that constitute most of rosin, the solid portion of the oleoresin of coniferous trees.

Pimaric acid is a carboxylic acid from the resin acid group. It can be prepared by dehydration of abietic acid, which it usually accompanies in mixtures like rosin.



abietic acid



pimaric acid

Remarks:
"Rosin "is a solid form of "resin", which is obtained from pines and some other plants, mostly conifers and is produced by heating fresh liquid resin to vaporize the volatile terpene components (www://en.winkipedia.org/wiki//Rosin).
"Rosin" is the residue left distilling of the volatile oil from oleoresin contained from *Pinus palaustris* (Longleaf pine) and other species of *Pinus in the family* Pinacae. Rosin is not a single, unique chemical substance but rather of a mixture of resin acids (e.g. abietic and palustric acid).

A source of rosin includes rosin (called *Tall Oil rosin*) obtained from the distillation of Crude Tall Oil (CTO). Crude Tall Oil is a by-product obtained from the Kraft paper making process. Additionally rosin may be obtained from aged pine stumps. This type of rosin is typically called wood rosin. In this process, aged wood stumps are chipped and soaked in a solvent solution. The solvents are recovered along with the rosin, fatty acids, turpentine, and other constituents through distillation.

Unsaponifiables
Unsaponifiables are neutral compounds (include hydrocarbons, higher alcohols and sterols) which do not react with sodium hydroxide to form salts, and thus cannot be turned into "soap".

II. Tall Oil and chemicals closed related to Tall Oil

A. General

A group of chemicals all closely related to Tall Oil, which is a by-product from the alkaline pulping of wood, especially pinewood were analyzed. The Pine Chemicals Association, Inc. (PCA) has elected to treat these chemicals as a category for purposes of the HPV program, taking in consideration the facts that all of them are similar in chemical composition, being predominantly the extractives that remain after the pulping of wood. It is important to mention that all category of Tall Oil and related substances (substances derived from or closely to Tall Oil) are chemically complex, with their composition dependent on the source of the trees from which they were derived and the conditions under which the Tall Oil was distilled. Tall Oil fatty acids and their derivatives are all complex mixtures (Class 2 substances) derived from a natural product. Each species of pine tree has a somewhat different mix of fatty acids, and even within a species, the mix of fatty acids could be influenced by the climate and local terrain.

This group of chemicals consists of the following:
8002-26-4, Tall Oil
8016-81-7, Tall Oil Pitch
68140-16-9, Tall Oil Pitch, sodium salt
68152-92-1, Tall Oil, disproportionated
65997-01-5, Tall Oil, sodium salt
68647-71-2, Tall Oil, potassium salt
65997-02-6, Wastewater, Tall Oil soap acidulation

(**Attachment 6, section 8:** Pine Chemical Association, Atlanta: High Production Volume Chemical Challenge Program, and Attachment **7, section 8**: U.S. Environmental Protection Agency September 2008 Risk -Based Prioritization

Document: **Initial** Risk-Based Prioritization of High Production Volume Chemicals Tall Oil and Related Substances Category) .

B. Description of Tall Oil and Related Substances and Composition

Information on their composition, uses and the challenges of chemical analysis of these complex mixtures is described below:

B.1. Tall Oil (CAS# 8002-26-4)

The TSCA Inventory (Toxic Substances Control Act, TSCA) describes Tall Oil as, *complex combination of Tall Oil rosin and fatty acids derived from* ***acidulation of crude Tall Oil soap*** *and including that which is further refined. Contains at least 70% rosin.* " The two types of Tall Oil covered by this description are ***crude Tall Oil*** **and** ***distilled Tall Oil.***

B.1.1.Characterization of crude Tall Oil chemical composition

Conform to published data **(Attachment 2,section 9**: Koski, Anna, Applicability of crude Tall Oil for wood protection Faculty of Technology, Department of Process and Environmental Engineering, University of Oulu, University of Oulu, Finland ,Acta Univ. Oul. C 293, 2008),the dark-colored crude Tall Oil (CTO) is not composed of pure triglycerides like other vegetable oils, but is rather a mixture of fatty acids, rosin acids and unsaponifiable substances, e.g. sterols, waxes and hydrocarbons.
Several carboxylic acids, fatty acids and rosin acids are found in crude Tall Oil. The predominant fatty acids, contributing the bulk of the observed physical and chemical properties, are oleic and linoleic acids (Duncan 1989), whereas the main resin acids are abietic-type acids and pimaric-type acids (Soltes & Zinkel1989), CTO varies considerably in composition and quality depending on the location of the mill, time of year, growing cycle of the tree, tree species, ageing of the wood,amount of heartwood, pulping conditions, handling and storage of the wood and the efficiency of the system used to recover the Tall Oil (see Drew & Propst 1981, Gullichsen & Lindeberg 1999).

References cited but not submitted:

Duncan DP (1989) Tall Oil fatty acids. In: Zinkel DF & Russel J (eds) Naval stores: Production, chemistry and utilization. Pulp Chemical Association, New York, US: 346-439.

Soltes EJ & Zinkel DF (1989) ,Chemistry of rosin. In: Zinkel DF & Russel J (eds) Naval stores: Production, chemistry and utilization. Pulp Chemical Association, New York, US.: 261-345

Drew J & Propst M (1981) Tall Oil: A book on the processing and use of Tall Oil; for Chemists, engineers, managers and producers. Pulp Chemicals Association, New York, US

B.1.2.*Crude Tall Oil* and *distilled* composition

The actual composition of both types of Tall Oil (crude and distilled) can vary widely.

The composition of a typical crude Tall Oil produced in the southeastern U.S. and a typical distilled Tall Oil are given in Table 2.

Table 2

Composition of Typical Tall Oils

	Crude Tall Oil	**Distilled Tall Oil**
Acid number	165	185
Fatty acids (%)	52	65
Resin acids (%)	40	30
Unsaponifiable matter (%)	8	5

(**Attachment 6, section 8** Pine Chemical Association, Atlanta: High Production Volume Chemical Challenge Program, Test Plan for Tall Oil and Related Substances,Submitted to US EPA and **Attachment 1, section 8**: Zinkel and Russell 1989, Naval Stores Research at the Forest ProductsLaboratory,NavalStoresReview97 (1):5-8(1987). By Duane F. Zinkel *Forest Products Laboratory, Forest Service, U.S. Dept. of Agriculture One Gifford Pinchot Drive, Madison, WI 53705-2398*)

The composition of crude Tall Oil depends on the species of tree from which it was derived, while the composition of distilled Tall Oil depends upon the species of tree as well as the processing conditions under which it was manufactured.
Information on the composition of the Tall Oil is provided in Table 3 (HPV Test Plan and Robust Summary for Tall Oil and Related Substances, submitted to the USAEPA by Pine Chemical Association)

Table 3 Composition of Distillated Tall Oil

Palmitic acid	$CH_3(CH_2)_{14}COOH$	3%
Palmitoleic acid[a]	$CH_3(CH_2)_xCH=CH(CH_2)_yCOOH$	1%
Stearic acid	$CH_3(CH_2)_{16}COOH$	1%
Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	28%
Linoleic acid	$CH_3(CH_2)_4CH=CH\text{-}CH_2CH=CH(CH_2)_7COOH$	19%
Linoleic acid, conjugated[b]	$CH_3(CH_2)_xCH=CHCH=CH\text{-}(CH_2)_yCOOH$	9%
Other fatty acids[c]		7%
Isopimaric acid		3%
Abietic acid		10%
Dehydroabietic acid		5%
Other resin acids		11%

---

a: x+y= 12

b: x usually 4 or 5 y usually 7 or 8, but x + y = 12

c 5,9,12-octadecatrienoic acid, linolenic acid, 5,11 14-eicosatrenoic acid, cis,cis-5,9-octadecadienoic acid; eicosadienoic acid elaidic acid; cis-1 1 octadecanoic acid; C-20, C-22, C-24 saturated acids.

B.2. Tall Oil Pitch (CAS# 8016- 81-7)

Tall Oil pitch is a tarry semi-solid material with a composition very dependent on the processing conditions under which it was produced. It has a low acid number and a complex composition.

The TSCA Inventory defines Tall Oil pitch as ***"the residue from the distillation of Tall Oil. It contains primarily high boiling esters of fatty acids and rosin. It may also contain neutral materials, free fatty acids and resin acids".***

Pitch is primarily made up of high boiling, high molecular weight compounds formed at the high temperatures encountered during the fractionation process. These compounds include the esters of fatty acids and rosin, and small amounts of dimmers and trimers of resin acids and fatty acids. Because pitch has such an extremely complex and variable composition, chemical analysis is not possible, and no typical composition can be presented.

B3. Tall Oil Pitch, Sodium Salt (CAS# 68140- 16-9)

This substance is made by neutralizing Tall Oil pitch with sodium hydroxide. It is sold as an aqueous dispersion.

B4.Tall Oil, Disproportionated (CAS# 68152-92-I)

Disproportionated Tall Oil is distilled Tall Oil that has been heated with a catalyst that removes conjugated double bonds. The fatty acid and resin acid contents of the treated product are the same as the **starting distilled Tall Oil** (see Table Composition of Typical Tall Oils), but some of the individual components are changed.

Composition of Typical Tall Oils

	Crude Tall Oil	Distilled Tall Oil
Acid number	165	185
Fatty acids (%)	52	65
Resin acids (%)	40	30
Unsaponifiable matter (%)	8	5

For example, abietic acid is converted to dehydroabietic acid and linoleic acid is converted to oleic acid.

B5. Fatty Acids, Tall Oil (CAS# 61790-12-3)
The composition of a typical Tall Oil fatty acid (TOFA) is shown in the following

Table 4 Composition of a Typical Tall Oil Fatty Acid

Chemical %	***Name Structure***	***Composition***
1	CH3(CH2)14COOH	Palmitic acid
2	CH3(CH2)16COOH	Stearic acid
48	CH3(CH2)7CH=CH(CH2)7COOH	Oleic acid
35	CH3(CH2)4CH=CH-CH2CH=CH(CH2)7COOH	Linoleic acid
7 4	CH3(CH2)XCH=CHCH=CH-(CH2)YCOOH	Conjugated linoleic acid
		Other acids
		Unsaponifiable matter

B6. Tall Oil, Sodium Salt (CAS # 65997-01-5) and **Potassium Salt(CAS # 68647-71-2)**
The sodium salt of crude Tall Oil is also known as Tall Oil soap, the precursor to Tall Oil.
Both the sodium and potassium salts of Tall Oil are also produced from *distilled Tall Oil.*
The salts are made by treating Tall Oil with the appropriate base and dispersing the salt formed in water. These compounds, as the salts of a strong base and a weak acid, result in alkaline dispersions with the pH dependent on the salt concentration in the dispersion.

B7. Wastewater, Tall Oil Soap Acidulation (CAS # 65997-02-6)
The TSCA Inventory defines this byproduct as, *"The aqueous layer formed by acidulation of Tall Oil soap with sulfuric acid during the production of Tall Oil. Composed primarily of a solution of sodium sulfate, the remainder being lignin and Tall Oil.* " Typically, Tall Oil soap acidulation wastewater is about a 12% solution of sodium sulfate, containing about 1 to 2% Tall Oil.

C. Methods of analysis for Tall Oil Product and chemical closed to Tall Oil

Analytical values which are often determinate on crude Tall Oil, acid-refined Tall Oil, distilled Tall Oil and Tall Oil fatty acids are the follows:
-*Chemical values:* Acid number, Saponification number ,rosin acids ,fatty acids, unsaponifiable, polyunsaturated fatty acids (conjugated and total linoleic acid),saturated faty acids,oleic acid and iodine value.

(**Attachment 3,section 9 :** Richard Herrlingen , Method of analysis of Tall Oil Product, Journal of the American Oil Chemists Society,Volume 36,Number 3/March 1959)

The most characteristic analyses: are *Acid number* or their overall *fatty acid* or *resin acid content.*

-*Physical values:*
Color, moisture, specific gravity, refractive index, viscosity, flash point, pour point, cloud, and titer.

All the substances in the category of Tall Oil and related to Tall Oil group of chemicals are chemically complex, they are not described in terms of their chemical composition, but only in general terms such as their acid number or their overall fatty acid or resin acid content (Zinkel and Russell 1989**).** However, some general information on the typical composition of each of the seven substances in this category are provided.
(**Attachment 1, section 8:** Final Submission for Tall Oil and Related Substances Zinkel, D.F. and Russell, J., Eds. 1989. Naval Stores Production, Chemistry , Utilization. Pulp Chemicals Association, New York.)

Most of analytical methods for Tall Oil are established standards as such, collected in ASTM and especially in Pulp Paper publications.
In addition to the standard methods of analyses, gas – liquid chromatography, mass spectroscopy and gel permeation chromatography are used widely for better understanding of Tall Oil chemistry.

Published data: The quality of the Tall Oil is monitored by using the *acid number.* This is a measure of the total acid (i.e. fatty and resin acids, so long as there is no excess of sulphuric acid) content of the crude Tall Oil. It is determined by ordinary titration with KOH, and is expressed as mg KOH/g sample. This is a sufficiently good measure of the quality of the oil for those at Kinleith(Pulp, paper, plywood, and wood processing centre in North Island, New Zealand) but the users of the oil have more sophisticated procedures.
The non-saponifiables are obtained from aqueous solution of the saponifiables by solvent extraction. The acids are analyzed for by acidification of the solution, causing the acids to precipitate, followed by solvent extraction and then quantitative gas chromatographic analysis.

References:
Attachment 6,section 9: Heather Wansbrough, Methods of Analysis for Tall Oil,Arizona Chemical Company ,Panama City,Florida based on two articles by P.J. Hooker and L.E. Fotherby (1977 Chemistry) (1977 Chemistry) and by Malcolm Rough, Senior Process Engineer, KRTA Ltd. respectively, with updated information provided by Stuart Cooney (Eka Chemicals) and with reference to:Grant, Roger and

Grant, Claire; *Grant and Hockh's Chemical Dictionary (5th ed.)*;McGraw-Hill Book Company; 1987)

Tall Oil fractionation products such as Tall Oil fatty acids, *distilled Tall Oil*, and Tall Oil rosin are routinely analyzed by gas chromatography (GC) after derivatization with diazomethane or esterification with methanol using boron trifluoride as a catalyst. An alternative derivatizing reagent, N,N-dimethylformamide dimethylacetal, has been investigated for the preparation of methyl esters of fatty acids and resin acids in Tall Oil fractionation products prior to GC analysis. This reagent provides a safe, rapid, and reproducible means of derivatization that eliminates the need to isolate the methyl esters from the derivatization reaction mixture.

(Attachment 8 ,section 9 : Gas chromatographic analysis of Tall Oil fractionation products after methylation with N,N-dimethylformamide dimethylacetal ,MCGUIRE J. M. (1) ; POWIS P. J. (1) , Journal of chromatographic science ISSN 0021-9665 CODEN JCHSBZ , 1998, vol. 36, n°2, pp. 104-108).

A gas chromatogram of Tall Oil rosin is shown in Figure below.

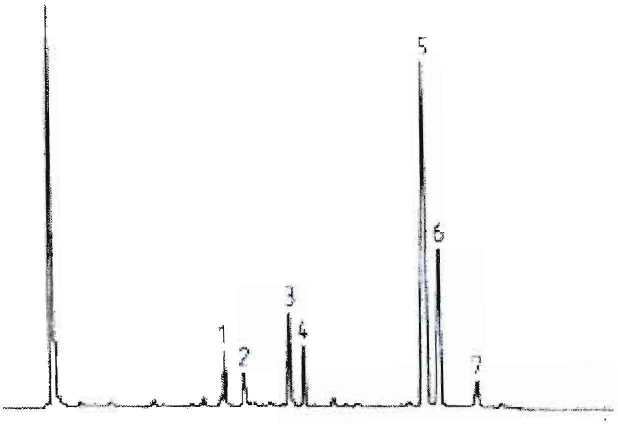


Figure 1 . Gas chromatogram of Tall Oil rosin
1. Pimaric acid; 2. Sandaracopimaric acid; 3. Palustric acid;
4. Isopimaric acid; 5. Abietic acid; 6. Dehydroabietic acid;
7. Neoabietic acid

These methods are essentially necessary complements to the older standard analyses for further development of the processes and of special or unique products as well.

Typical data and composition of Tall Oil fatty acids and of Tall Oil rosins are listed in Tables 1 and 2

Table 1. Typical data and composition of Tall Oil fatty acids and of Tall Oil rosins

		Scandinavia	United States
Acid number		195	197
Rosin acids, %		2	1
Unsap a, %		2	1.5
Iodine value		130	130
Color, Gardner		4	5
Fatty acids, %			
Saturated		2	2
Oleic	(18:1)	30	48
Linoleic	(18:2)	44	37
Linolenic	(18:3)	10	5
Conjugated	(18:2)	6	5
Other		4	2.5

a Unsaponifiables.

Table 2. Typical data and composition of Tall Oil fatty acids and of Tall Oil rosins

	Gum rosin	Wood rosin	Tall oil rosin		
			United States	Scandinavia	
				I	II
Acid number	167	157	174	173	170
Rosin acids, %	90	85	92	90	95
Fatty acids, %			3	4	2
Softening point, °C	78	73	75	66	75
Color, USDA a			"WW"	X	XA
Composition of rosin acids fraction, %					
Pimaric	7	7	2	3	3
Palustric	20	8	7	8	7
Isopimaric	15	15	8	6	6
Abietic	30	50	42	45	40
Dehydroabietic	5	8	20	22	25
Neoabietic	15	5	3	4	4

Table 3.Application of Tall Oil fractions

Composition uses	Pitch	Rosin	Distilled tall oil	Fatty acids	Heads
Principal composition	esters, sitosterol, estolides, rosin dimer, free fatty and rosin acids	rosin acids (isomeric diterpene acids, complex mixture), free fatty acids, neutrals, unsap 3 – 10 %, esters	fatty and rosin acids, neutrals, unsap, esters < 10 %	fatty acids (oleic, linoleic type) (> 90 %), rosin acids (neutrals < 10 %)	fatty acids (saturated)
As intermediates in miscellaneous processes	mixtures for chemical modification	fortification, Diels – Alder reaction, dimerization (catalytic process), isomerization, esterification, disproportionation	alkyd formation, esterification, saponification, epoxidation	dimerization, isomerization, esterification, alkyd formation, saponification, separation, ethoxylation, decarboxylation, C_{21} diacids	mixtures, crystallization (palmitic acid)
Final uses	fuel, binders, coatings, rubber modifier, asphalt, sizing, printing inks, hardboard impregnation	paper size, protective coating, adhesive, ink, rubber, hot melt	soap, coating, flotation, board impregnation	protective coating, soap, ink	fuel, flotation, asphalt emulsifier

Tall Oil fractionation capacity by company is given in Figure 2

World Tall Oil fractionation capacity by company

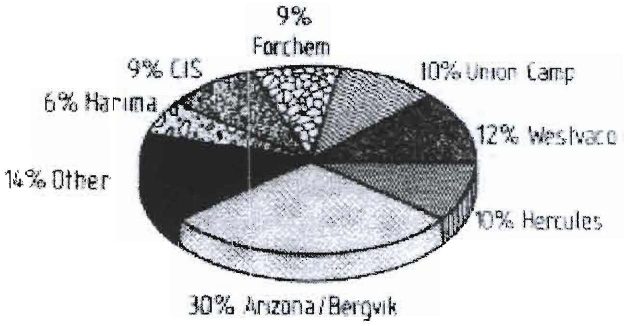


Figure 2. World Tall Oil fractionation capacity by company

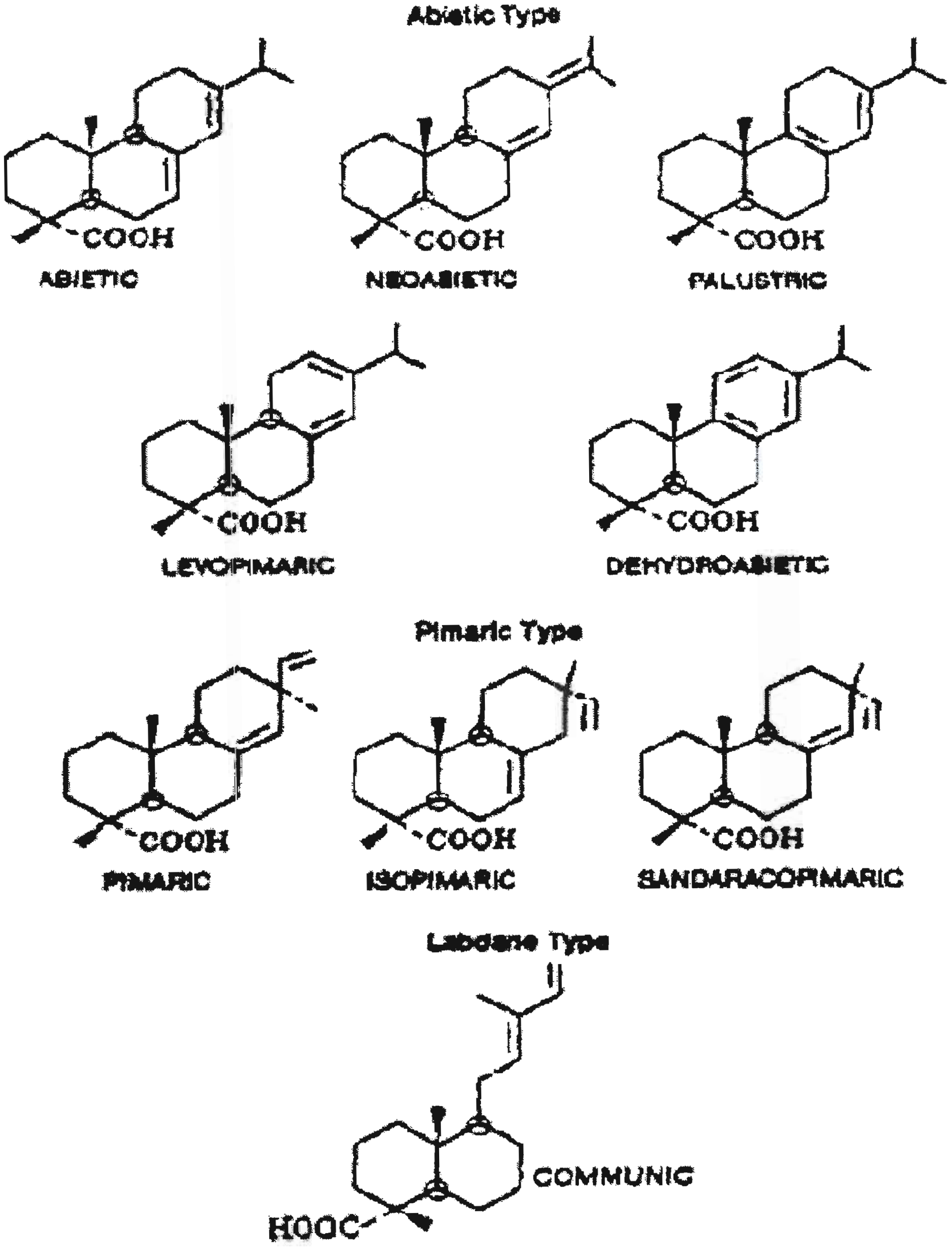
Reference: Attachment 7, section 9: article "Tall Oil", Lars-Hugo Norlin, Bergvik Kemi, Sandarne, Sweden, 2005

Other References, publications of the Tall Oil laboratory:

- Soltes and Zinkel, "Chemistry of Rosin," Zinkel and Russell (eds.), in Naval Stores: Production, Chemistry, Utilization, Pulp Chemicals Association, NY, 1989, Chapter 9, pp. 261-345
- Duncan, D., "Tall Oil Fatty Acids," Zinkel and Russell (eds.), in Naval Stores: Production, Chemistry, Utilization, Pulp Chemicals Association, NY, 1989, Chapter 10, pp. 346-439
- Burke, R., "Rosin-based Printing Inks," Zinkel and Russell (eds.), in Naval Stores: Production, Chemistry, Utilization, Pulp Chemicals Association, NY, 1989, Chapter 19, pp. 665-70

D. Structures of some representative resin acids found in distilled Tall Oil and its derivatives are shown in Figure 1.

Figure 1



Common Resin Acids

E. Other chemical general considerations for analyzing group of chemicals all closely related to Tall Oil

All of the substances in the previously presented category (group of chemicals closed related to Tall Oil) are Class 2 substances. The fact that this are complex combinations, and also that Tall Oil is essentially insoluble in water and decomposes on heating at high temperature, may creates a variety of analytical issues.
Gas chromatography of methylated derivatives is the accepted method for the analysis of the members of this category.
Pine Chemical Association has verified the reliability of the standard analytical methods at low concentrations (at which the very low solubility of Tall Oil is known - about 10 ppm).
Class 2 substances are composed of a complex mixture of substances and are often difficult to characterize (as noted above). Their composition is variable and not be represented by a definite chemical structural diagram. Due to this "complex mixture" characteristic of Tall Oil and related compounds, some physical property measurements, such as the partition coefficient are of questionable value because the methodology used to determine these properties will actually fractionate or partition the substances into various components.

Ea. Melting Point

Tall Oil and the other non-salts in this grouping category are liquids at room temperature; Tall Oil pitch is a semi-solid. A sharp melting point cannot be obtained for any of these compounds due to the complex nature of these substances. The salts are solids under ambient conditions and heating them to determine the melting point would cause thermal decomposition.

E b. Boiling Point

All of the non-salt members of this category are produced by high temperature, high vacuum distillation and are non-volatile at ambient temperatures. A boiling point at ambient pressure has no significance because when heated to high temperatures these materials will thermally decompose before they boil. The two salts in this category are solids. When heated to high temperatures, they will also thermally decompose before boiling. Accordingly, measurement of this property is inappropriate for all the substances in this category.

Ec. Vapor Pressure

Vapor pressures for Tall Oil and the other chemicals in this category at ambient temperatures are effectively zero, and their experimental measurement is inappropriate. The salt members of the category are solids and thus have no vapor pressure, so this end point cannot be measured. When dissolved in water, their solutions will reflect the vapor pressure of the water rather than the salt, and therefore measurement of this property is inappropriate.

Ed. Water Solubility

The water solubility of five compounds in this category will be determined using OECD protocol (105). The lack of a suitable analytical method for Tall Oil pitch precludes the determination of the water solubility.

E e. Partition Coefficient

Because all of these substances are Class 2 mixtures, the procedure (OECD 107) to determine the K,, often yields a number of separate K,, values rather than a single value representative of the mixture. Thus, the results will represent the partition coefficients of the components rather than the mixture.

(**Attachment 6, section 8:** Pine Chemical Association, Atlanta: High Production Volume Chemical Challenge Program, Reference: Zinkel, D.F. and Russell, J., Eds. 1989. Naval Stores. production, chemistry, utilization. Pulp Chemicals Association, New York and **Attachment 7,section 8:** U.S. Environmental Protection Agency September 2008 Risk -Based Prioritization Document :Initial Risk-Based Prioritization of High Production Volume Chemicals Tall Oil and Related Substances Category)

F. Summary of Physicochemical Properties tested for group of chemicals related to Tall Oil

Water Solubility

The water solubility of Tall Oil, disproportionated Tall Oil and two of the salts was determined.
The partition coefficients for six members of this category will be determined.
Adequate data exist for Tall Oil and pitch although both will be retested with the other compounds in this category.
Tests for the melting point, boiling point and vapor pressure are inappropriate.

The water solubility of all six compounds in this category was determined using OECD (105) with the results shown in Table 5.

Table 5

Water Solubility (mg/l)	Chemical
12.6	Fatty acids, Tall Oil
22.8	Fatty acids, Tall Oil, low boiling
15.0	Fatty acids, C16 - C18 and C18 unsaturated, branched and linear (monomer)
2.5	Octadecanoic acid, branched and linear
Miscible	Fatty acids, Tall Oil, potassium salts
Miscible	Fatty acids, Tall Oil, sodium salts

Water Solubility

The water solubility of all six compounds in this category was determined using OECD (105) with the results shown in Table 6.

Table 6 Water Solubility (mg/l)	Chemical
12.6	Fatty acids, Tall Oil
22.8	Fatty acids, Tall Oil, low boiling
15.0	Fatty acids, C16 - C18 and C18 unsaturated, branched and linear (monomer)
2.5	Octadecanoic acid, branched and linear
Miscible	Fatty acids, Tall Oil, potassium salts
Miscible	Fatty acids, Tall Oil, sodium salts

Physicochemical property – Octanol/Water Partition coefficient results:

TALL OIL CAS # 8002-26-4

1. At pH 2, the log P_{ow} [K_{ow}] values of eight components in Tall Oil were 6.1, 6.5, 7.0, 7.4, 7.6, 7.8, 8.1, and 8.2.
At pH 7.5 the log K_{ow} values of five components in Tall Oil were 3.5, 4.2, 4.5, 4.7, and 5.4.

Reference: Determination of log P_{ow} for single components in distilled Tall Oil. GLP Study No. 408335/475.Water Quality Institute, Horsh)lm, Denmark.
GLP Study No. 408335/473.
Testing was conducted according to OECD Test Method
117, "Partition Coefficient (n-Octanol/Water) High Performance Liquid Chromatography (HPLC) Method
Attachment 4, section 9: Dybdahl, H.P. 1993. Determination of log P_{ow} for single components in Tall Oil pitch.

2. For petitioned product Distillated Tall Oil for 20X, see below, under Chemical properties for our petitioned Tall Oil the attached documents* (see below) includes the physical –chemical properties .

***Attachment 5:** Safety Data Sheet Distilled Tal oil 20X (Forchem) and **Attachment 1, section 9**: Product data sheet Forchem)

Physical -Chemical properties results for our petitioned
Tall Oil CAS # 8002-26-4 are reported with the following values :

-Physical state, colour and odour): Liquid, yellow, faint odour

-Solubility

- **Water solubility:** Not soluble
- **Fat solubility**: Soluble

-Viscosity: 80 Cp (20° C) 80

Analysis	Typical Value	Method
-Acid Value, mg (KOH)/1g	192	4ASTM D 465-01
-Flash Point, closed cup, ° C	200	SCAN 6:67
-Cloud point, ° C	-1	ASTM D 2500-99
-Free Fatty Acid, %	75	ASTM D 1585-96
-Free Rosin Acid, %	20	SCAN-T 14:78
-Color Garner (Photometer)	4.5	ASTM D 6166-97

-Saponification Value	194	SCAN-T 12:72
-Pour Point, ° C	-6	SCAN-T 5:67
-Viscosity at 20° C, mPa s(Cp)	80	ASTM D 2196-99
-Refractive index, n 0 at 20° C	1.485	SCAN-T 1:65
-Unsaponifiables, %	3	SCAN-T 13:74

- Partition coefficient n-octanol/water: $\mathrm{Log_{10}P_{ow}}$ 3.5 - 8.2

III .Chemical interaction of Tall Oil with other substances

The ingredient (Tall Oil) in pesticide product, especially when is used in organic production, is not expected to interact with other chemicals and only it serve as a solvent/emulsifier.

The following information in support of the **chemical mode of action for Tall Oil**:

Tall Oil is used to make in formulated product as Timorex Gold .The pesticide active ingredient (fungicide) is mixed with this inert ingredient (Tall Oil), to obtain an emulsifiable formulation. Tall Oil is an emulsifier-solvent in our product – it interacts with sodium hydroxide and creates natural soap that makes it possible to our active ingredient to dissolve in water and allow us to formulate our A.I as EC formula.

Degradation of Tall Oil-studies

1. Study 1: In published data there are information about Tall Oil degradation held under heated conditions.

The degradation of model components of crude Tall Oil (**CTO**) held under storage conditions was studied.
Rate constants for the reactions of stearyl alcohol and mixed sterols separately and in combination oleic acid were determined. The rate of esterification between oleic acid and stearyl alcohol was found to be about three times faster than that of the reaction between oleic acid and Tall Oil sterols.

Attachment 9, section 9: Al Wong,Arbokem Ink.,Vancouver,Canada,Cellulose Chemistry and Technology,36:388-37-88(2002):Degradation of crude Tall Oil held under heated conditions. Part1 Basic reactions and mixtures of model compounds Al Wong ,Arbocem Ink.,Vancouver,Canada ,Forest Chemicals Review,113(2):12-16,2003)

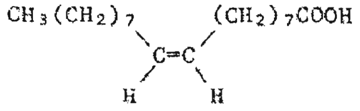
2. Study 2: Acid number deceases of ternary mixture of CTO model compounds, fatty alcohol ,sterol and fatty acid study were studied and was established a practicable means to estimate the rate and magnitude of acid number losses of Tall Oil during heated storage.

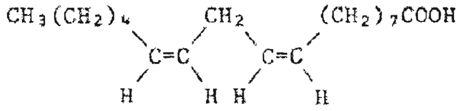
(**Attachment 10 section 9 :**Wong ,Arbocem Ink.,Vancouver,C0anada , Basic reactions and mixtures of model compounds AI ,Part 2 :Ternary mixture of model compounds and prediction of acid number decrease, Forest Chemicals Review,113(3):11-14,2003),page 3

IV. Reaction with Tall Oil (reactivity)

Presented data is based on published data.
1. The Degradation of Tall Oil Fatty Acids by Molecular Oxygen in Alkaline Media was described in published data , thesis submitted by Gerald R. Mittet B.S. 1972 University of Washington M.S. 1974 Lawrence University, Publication Rights Reserved by The Institute of Paper Chemistry January, 1979. (Attachments 11 and 12)
An investigation was undertaken to system reactions of Tall Oil fatty acids with oxygen and alkali under conditions stimulating those of oxygen-alkali delignification.
Five reactions variables studies were temperature, oxygen pressure, alkali and substrate. Only the reactions of fatty acids, which constitute one of the important fractions of *crude Tall Oil,* were examined.

The reactions of Tall Oil fatty acids and their esters with molecular oxygen and alkali were investigated under conditions chosen to simulate those which might be encountered in an oxygen-alkali delignification process (paper chemistry Industry). The primary objective of the investigation was to determine those reaction conditions most compatible with recovery of the fatty acids. Another objective, complementary to the first, involved identification of the fatty acid oxidation products and measurements of their yields.
The product analyses were intended to account for the fatty acid losses which did occur, and to obtain some understanding of the fatty acid oxidation mechanisms.
Tall Oil fatty acids occur in wood predominately as triglyceride esters, with lesser quantities as sterol esters or waxes. The two most abundant fatty acids are oleic acid (cis-9-octadecenoic acid) and linoleic acid (cis,cis-9,12- octadecadienoic acid).
In pinewood these two unsaturated compounds


Oleic Acid


Linoleic Acid

$CH_3(CH_2)_{14}COOH$

Palmitic Acid

are found in approximately equal quantities and together account for about 80% of all the fatty acids.
The third most abundant fatty acid is palmitic acid (hexadecanoic acid), a saturated acid which accounts for about 6% of all fatty acids in pine. The remaining fatty acids are saturated and unsaturated compounds of varying chain lengths and varying degrees of unsaturation.
The reaction of molecular oxygen with neat fatty acids under mild conditions have been investigated.

Auto oxidation of fatty acids

All of the fatty acids found in wood are susceptible to reactions with the molecular oxygen present in air; under ambient conditions such reactions are commonly termed autoxidations. Auto oxidation refers to any reaction involving molecular oxygen.
Olefin autoxidation was the subject of extensive research conducted under the direction of the British Rubber Producers Research Association.

The kinetics and mechanism of autoxidation were elucidated during those investigations, and the results have been discussed in reviews by Bolland and by Bateman(literature cited in the Mittet's degradation study).

The mechanism of autoxidation which was proposed at that time, and which is still generally accepted, is represented by Equations (1) through (6).

Initiation RH + I (Initiator) -- R' + IH (1)
Propagation RRO.O -+ 0+2 RH - RROOOO H + R, ((2,3))
R- + R. -- "Inert" (4)
Termination R- + ROO- - Products (5)
ROO- + ROO0 - (6)

The mechanism outlined is a radical chain reaction. Autoxidation may be initiated by any species which will induce cleavage of carbon-hydrogen bonds.

Common initiators include free radicals and ultraviolet light. In the first step of the sequence a hydrogen atom is abstracted by the initiating species, yielding a chain-propagating free radical (R-). An allylic hydrogen atom is usually abstracted preferentially from unsaturated compounds, since the resulting free radical is resonance-stabilized. The free radical rapidly combines with oxygen to produce a peroxy radical as shown in Equation (2).

The peroxy radical abstracts a hydrogen atom from a second reactant molecule, yielding another reactive free radical and a hydroperoxide, as represented by Equation(3).

Reactions (2) and (3) are defined as chain-propagating steps, since in each case a radical is formed which may directly or indirectly initiate further oxidation. Under mild conditions hydroperoxides are the end products of autoxidation, which is terminated when the free radicals decompose to form products incapable of initiating or propagating further reaction, as indicated by Equations (4)-(6).

For autoxidation, the chain length is defined as the number of times Reactions (2) and (3) will occur before the sequence is interrupted by a termination reaction. At relatively high oxygen pressures the rates of the termination steps, (4) and (5), become insignificant compared to the rate of propagation step, (3), and termination occurs almost exclusivelyby Reaction (6).

Under suitable reaction conditions, and in the absence of pro- or antioxidants, autoxidation may be characterized by long chain lengths and high yields of hydroperoxides.

The autoxidation of fatty acids and fatty acid derivatives may also be described by the general mechanism of autoxidation shown in Equations (1) through (6).

In fact, esters of oleic acid and linoleic acid were commonly used as model compounds in many of the studies dealing with general olefin autoxidation. Numerous investigations by many different groups of workers have been directed specifically to the autoxidation reactions of fats and oils.

Most of this work was undertaken to clarify the chemistry associated with the development of rancidity in cooking oils and the polymerization of drying oils.

In most instances, the initial stages of autoxidation were adequately described by the radical chain mechanism.

Attachment11,section 9 : Gerard R.Millet and Norman S.Thomson ,The reaction of Tall Oil Fatty Acids , the Institute of Paper Chemistry, Appleton, WISCONSIN, may, 1979

Attachment12,section 9 : Degradation of Tall Oil Fatty Acids by Molecular Oxygen in Alkaline Media ,The Institute of Paper Chemistry ,Gerrald R. Mittet

2.In on other study (attachment 13,section 9) it is presented that Diene fatty acids (as Tall Oil acids)are dibasic and react with diamines and triamines to give polyamides.

Attachment13, section 9: Charlie Scrimgeour, Scottish Crop Research Institute, Dundee ,Scotland, Chemistry of Fatty Acids

(b) Toxicity and environmental persistence

As Part of the High Production Volume (HPV) Program , the Pine chemicals Association, Inc. has sponsored 6 HPV chemicals . The final summary (final submission to the EPA) addresses the following six chemicals, known collectively as Tall Oil Fatty Acids and Tall Oil Fatty Acid Salts, available data show Tall Oil (CAS no. 8002-26-4) is non-toxic in acute studies and indicate that the material is dominated by readily biodegradable compounds . The inoculum had satisfactory activity as demonstrated by more than 60% degradation activity as demonstrated by more than 60% within 7 days using the reference compound and in another study 73 % of Tall Oil was biodegraded after 28 days indicating that the organic portion of test material was inherently biodegradable:

8002-26-4, Tall Oil
8016-81-7, Tall Oil Pitch
68140-16-9, Tall Oil Pitch, sodium salt
68152-92-1, Tall Oil, disproportionated
65997-01-5, Tall Oil, sodium salt
68647-71-2, Tall Oil, potassium salt
65997-02-6, Wastewater, Tall Oil soap acidulation

Acute Oral Toxicity Data of Tall Oil (CAS no. 8002-26-4):

Tall Oil (CAS no. 8002-26-4) was found non-toxic following acute oral exposure.

The acute oral toxicity of Tall Oil has been determined in two studies in rats. The acute oral LD50 was > 5000 mg/kg in one study and > 6000 mg/kg in another study.

Tall Oil has been tested for acute oral toxicity and found to be non-toxic (i.e. LD50 > 5000 mg/kg) , it is well above the guideline of 2000 mg/kg.

Attachment 14, section 9: High Production Volume (HPV) Chemical Challenge Program , Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. 2001 .

Acute oral, repeated oral dose toxicity and Ecotoxicity of Tall Oil related substances:

As Part of the High Production Volume (HPV) Program , the Pine Chemicals Association, Inc. (PCA) has sponsored 6 HPV chemicals . This final summary (final submission to the EPA) addresses the following six chemicals, known collectively as Tall Oil Fatty Acids and Tall Oil Fatty Acids Salts (61790-12-3 , Fatty acids, Tall Oil , 65997 -03-7, Fatty acids, Tall Oil, low boiling, 68955-98-6, Fatty acids, unsaturated, branched and linear, 68955-98-6, fatty acids, unsaturated, branched and linear, 68201-37-6 , octadecanoic acid, branched and linear, 61790-44-1, Fatty acids, Tall Oil, potassium salts, 61790-45-2 , Fatty acids, Tall Oil, sodium salts), all the members of this group are similar in chemical composition.

Although our Tall Oil (CAS no .8002-26-4) is not included in this document, all are related substances to Tall Oil, the chemicals in this group are derived from or closely related to Tall Oil fatty acids, a substance obtained by the fractional distillation of crude Tall Oil (CAS no. 8002-26-4).

Tall Oil Fatty Acids (TOFA) was tested in a 90 day subchronic toxicity study in rats.

The NOEL (No Observed Effect Level was 5% (approximately 2500 mg/kg/day), other subchronic studies for 28 and 40 days confirm the low toxicity of TOFA. TOFA and monomer acid, sodium salt are negative in the Ames test and clastogenic only at concentrations that were overtly toxic to the cells. No evidence of reproductive or developmental toxicity in a full –two generation study. Consequence, no adverse health consequences would be associated with any anticipated exposures to TOFA or related substances. The report shows that the human exposure are limited by the fact that most Tall Oil chemicals are industrial intermediates consumed in the production of other chemicals.

Toxicology for TOFA (Tall Oil fatty acid, CAS no. 61790-12-3) other substances from the same group of chemicals derived from or closely related to Tall Oil has no acute oral toxicity (i.e., LD50 > 10,000 mg/kg), and repeat oral dose toxicity data demonstrate a no observed effect level (NOEL) of approximately 2500 mg/kg/day.

This research demonstrates that both Tall Oil Fatty Acids and monomer acid are non-toxic to fish, daphnia and algae.

Attachment 15, section 9: High Production Volume (HPV) Chemical Challenge Program , Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. Aug. 2004.

Eye contact: Irritating

Ingestion: Oleic acid: LD50, oral-rat=74 g/kg. Linoleic acid:LD50, oral-rat>3,2 g/kg. Resin acid: LD50 oral-rat 7,6 g/kg; LD50 oral-mouse 4,6 g/kg.

Attachment 5, section 9: See Material Safety Data Sheet Distillated Tall Oil 20X, Forchem.

Repeat Dose Toxicity Data

Tall Oil Fatty Acid (CAS 61790-12-3) was tested in a 90-day subchronic toxicity study in rats. The test trials concentrations were 0,5,10 or 25% for 90 days. The approximate doses were 0, 2500, 5000 or 12500 mg/kg/day. The toxicity demonstrate a no observed effect level (NOEL) of approximately 2500 mg/kg/day

Reproductive and Genotoxicity

There was no evidence of reproductive or developmental toxicity in a full two-generation study. NOEL > 5000 mg/kg/d.

Mutagenicity

Test results show no evidence of mutagenicity in *Salmonella* (i.e., Ames test) for either TOFA (CAS no. 61790-12-3) or monomer acid sodium salt. Chromosomal aberrations in Chinese hamster ovary (CHO) cells were evident only at concentrations of TOFA that were overtly toxic to the cells;
Consequently, no adverse health consequences would be associated with any exposures to TOFA or related substances.

Potential exposure

With respect to potential exposure to the substances in this category, all are consumed almost entirely as industrial intermediates where they are reacted or further distilled to produce other chemicals. Of the various TOFA distillation and reaction products, it is estimated that greater than 75% are marketed and consumed in non-dispersive commercial applications in the production of dimer acids, polyamide adhesive resins, alkyd resins for paint, polyester lubricants, plasticizers, and metal working fluids. Volatilization to air and hence inhalation exposure would be minimal due to the essential lack of a vapor pressure for these substances. Exposure in all of these industrial applications is generally limited to dermal contact during manufacture of the numerous products derived from TOFA and related substances.

Attachment 15, section 9: High Production Volume (HPV) Chemical Challenge Program , Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. Aug. 2004.

Remark:
Tall Oil (CAS no. 8002-26-4) is known to be used as a pesticide (insecticide repellent). Recently this substance was approved by EFSA and included in the EU Annex 1 inclusion of the EU registration directive, EEC 91/414., attachment 6 section 7 , list of Annex 1.

Published 'Draft Assessment Report' of Tall Oil (CAS no. 8002-26-4) in European Food Safety Authority site: http://www.efsa.europa.eu/.

(c) Environmental impacts from its use and or manufacturer and (d) Effects on human health

Initial risk based preordination of high production volume chemicals, Tall Oil and related substances category, this document from September 2008, is based on screening –level characterization done by EPA on the environmental fate, hazard, and exposure of the listed chemicals. The information used by EPA includes data submitted under the HPV Challenge Program and the 2006 Inventory Update Reporting (IUR), and data availability through other selected sources.

Human health:

Available studies indicate that the acute oral toxicity for several members of this category is low. Tall Oil CAS no. 8002-26-4 was selected as representative of this category for testing the remaining endpoints. Repeated oral exposures in animal studies show low toxicity. There was no developmental toxicity and low reproductive toxicity, the Tall Oil CAS no. 8002-26-4 did not show mutagenic potential or induce chromosomal effects *in vitro* tests.

Exposure:

Potential Characterization Summary:

- Potential Risk Aquatic Organisms from Environmental Releases: Low concern. EPA identifies a medium potential that aquatic organism might be exposed from Environmental releases. All category members have low bioaccumulation potential and six of the eight members have low environmental persistence. These characteristics in combination with the low acute toxicity for fish, invertebrates and aquatic plants, suggest a low concern for potential risk to aquatic organisms.

- Potential Risk to General Population from Environmental Releases: Low concern. EPA identifies a medium potential that the general population might be exposed from environmental releases. The potential human health is expected to be low due to minimal toxicity in animals following repeated exposures at high doses. The available information suggests a low concern for potential risk to the general population from environmental releases.

- Potential risk to workers: Low concern. EPA identifies a medium relative ranking for potential worker exposure. The potential human health hazard is expected to be low.

- The available information suggests a low concern for potential risks to workers.

- Potential Risk consumers from known uses: Low concern. EPA identifies a high potential that consumers may be exposed. The potential human health hazards are expected to be low. A low concern suggests for potential risks to consumers.

- Potential risk to children – Low concern. EPA identifies a high potential that children may be exposed. Exposures to children may also be expected to occur through the household use of some consumer products. Available information suggested a low concern for potential U.

Attachment 7, section 8 : U.S. Environmental Protection Agency September 2008 Risk , Based Prioritization Document : Initial Risk-Based Prioritization of High Production Volume Chemicals , Tall Oil and related substances Category .

Remarks:

(1 Tall Oil (CAS no. 8002-26-4) is known to be used as a pesticide (insecticide repellent). Recently this substance was approved by EFSA and included in the EU Annex 1 inclusion of the EU registration directive, EEC 91/414.

Published 'Draft Assessment Report' of Tall Oil (CAS no. 8002-26-4) in European Food Safety Authority site: http://www.efsa.europa.eu/.

2) See HPV task force consortium registration, www.pinechemicals.org , as part of the High Production Volume (HPV) Program. This includes summary for crude Tall Oil and Distillated Tall Oil.

(e) Effects on soil organisms, crops, or livestock

Environment

Available data indicate that the potential acute hazard to fish, aquatic invertebrates and aquatic plants is low. Based on their environmental fate characterization the hazard to aquatic organisms under exposure conditions is expected to be low for all category members except two which are moderately persistent is expected to limit chronic toxicity (CAS no. 8016-81-7, 68140-16-9), Therefore, chemicals in this category have a low bioaccumulation potential.

Attachment 7, section 8: U.S. Environmental Protection Agency September 2008 Risk , Based Prioritization Document : Initial Risk-Based Prioritization of High Production Volume Chemicals , Tall Oil and related substances Category.

As Part of the High Production Volume (HPV) Program, the Pine chemicals Association, Inc. has sponsored 6 HPV chemicals. The final summary (final submission to the EPA) addresses the following six chemicals, known collectively as Tall Oil Fatty Acids and Tall Oil Fatty Acid Salts, available data show Tall Oil (CAS no. 8002-26-4) is non-toxic in acute studies and indicate that the material is dominated by readily biodegradable compounds . The inoculum had satisfactory activity as demonstrated by more than 60% degradation activity as demonstrated by more than 60% within 7 days using the reference compound and in another study 73 % of Tall Oil was biodegraded after 28 days indicating that the organic portion of test material was inherently biodegradable.

8002-26-4, Tall Oil
8016-81-7, Tall Oil Pitch
68140-16-9, Tall Oil Pitch, sodium salt
68152-92-1, Tall Oil, disproportionated

65997-01-5, Tall Oil, sodium salt
68647-71-2, Tall Oil, potassium salt
65997-02-6, Wastewater, Tall Oil soap acidulation

Attachment 14, section 9: High Production Volume (HPV) Chemical Challenge Program , Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. 2001 .

Photodegradation

Due to their low water solubility and lack of any vapor pressure at ambient temperatures, there is no opportunity for any of these chemicals to enter the atmosphere. Thus, photodegradation is irrelevant. In addition based on the constituents in these complex mixtures, there is no reason to suspect that they would be subject to breakdown by a photodegradative mechanism. Consequently, this endpoint will not be determined for any of the substances in this category.

Hydrolysis

Hydrolysis as a function of pH is used to assess the stability of a substance in water. Hydrolysis is a reaction in which a water molecule (or hydroxide ion) substitutes for another atom or group of atoms present in an organic molecule. If there is no group 15 suitable to be displaced, then the organic compound is considered to be resistant to hydrolysis. None of the substances in the Tall Oil category contains an organic functional group that might be susceptible to this physical degradative mechanism.

Therefore, hydrolysis need not be measured.

In addition, low water solubility often limits the ability to determine hydrolysis as a function of PH. All of the Tall Oil compounds have very low solubility in water. Therefore, these materials are expected to be stable in water and it would be unnecessary to attempt to measure the products of hydrolysis. With respect to the various Tall Oil salts, since they exist in an aqueous medium they hydrolyze (ionize) immediately, but form stable species. Consequently, it would also be unnecessary to measure this endpoint for Tall Oil salts.

Attachment 14, section 9: High Production Volume (HPV) Chemical Challenge Program , Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. 2001 .

Biodegradation

A GLP study was conducted according to OECD Test method 301 D" Ready Biodegradability' closed bottle test using Tall Oil (CAS no 8002-26-4).

The results show that degradation % after time is:

43% after 7 days (test article)

60% after 28 days (test article)

63% after 7 days (reference compound)

77% after 28 days. (reference compound)

The conclusion was that the biological oxygen demand for Tall Oil was 43 and 60% of the theoretical oxygen demand after 7 and 28 days, respectively. These data indicate that the material is dominated by readily biodegradable compounds, Tall Oil did not inhibit the respiratory activity of the inoculum. The inoculum had satisfactory activity as demonstrated by more than 60% degradation within the 7 days using the reference compound.

In another GLP study using Tall Oil (CAS no 8002-26-4), testing was conducted according to OECD test method 301 F, Manometric respiratory test for biological degradation. The results show that the degradation % after time were 73% after 28 days (test article) and 97% after 28 days (reference substance). The conclusion was that the 73% of Tall Oil biodegraded after 28 days indicating that the organic of the test material was inherently biodegradable. See table 1.

Table 1:

Chemical	**Method**	**Percent Biodegradation**
Fatty acids, Tall Oil (Test 1)	OECD 301D	56
Fatty acids, Tall Oil (Test 2)	OECD 301F	84
Fatty acids, Tall Oil (Test 3)	OPPTS 853.110	74
Fatty acids, Tall Oil, low boiling	OECD 301D	41
Fatty acids, C16 - C18 and C18	OPPTS 853.110	67
Octadecanoic acid, branched and linear	OECD 301B	47
Fatty acids, Tall Oil, potassium salts	OPPTS 853.110	79
Fatty acids, Tall Oil, sodium salts	OECD 302B	98

Attachment 14, section 9: High Production Volume (HPV) Chemical Challenge Program , Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. 2001 .

Ecotoxicity Data

Aquatic toxicity to Distillated Tall Oil:
Fish LC50 (96h) > 10 000 mg/l WAF (OECD 203)

Daphnia EC50 (48h) > 10 000 mg/l WAF (OECD 202)

Algae EC50 (72h) > 1000 mg/l WAF (OECD 201)

Toxicity to other organisms to Distillated Tall Oil:

NOEC > 1000 mg/l, Bacteria E50 > 10 000 mg/l WAF (ISO 10712). NOEC > 10 000 mg/l

Attachment 5, section 9: See Material Safety Data Sheet Distillated Tall Oil 20X, Forchem.

For other substances from the same group of chemicals derived from or closely related to Tall Oil :

Tall Oil Fatty Acid (TOFA) CAS no. 61790-12-3 was tested for acute toxicity to fish, daphnia and algae at the maximum measured water solubility.

Acute Fish 96 hours NOEL : 1000 mg/l

Acute Daphnia 48 hours NOEL: 1000 mg/l

Acute Algae 72 hours NOEL : 854 mg/l

The data on TOFA and monomer acid demonstrate that all of the substances in this group category are non-toxic to aquatic organisms including fish, daphnia and algae.

Fatty acids, CAS no. 68955-98-6 was tested for acute toxicity to fish, daphnia and algae at the maximum measured water solubility:

Acute Fish 96 hours NOEL : 1000 mg/l

Acute Daphnia 48 hours NOEL: 1000 mg/l

Acute Algae 72 hours NOEL : 1000 mg/l

The main conclusion ; Tall Oil and related substances are not toxic to aquatic organisms including : fish, Daphnia and Algae.

Attachment 15, section 9: High Production Volume (HPV) Chemical Challenge Program , Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. Aug. 2004

Attachment 7, section 8: U.S. Environmental Protection Agency September 2008 Risk , Based Prioritization Document : Initial Risk-Based Prioritization of High Production Volume Chemicals , Tall Oil and related substances Category

Remarks:

1) Tall Oil (CAS no. 8002-26-4) is known to be used as a pesticide (insecticide repellent). Recently this substance was approved by EFSA and included in the EU Annex 1 inclusion of the EU registration directive, EEC 91/414.

Published 'Draft Assessment Report' of Tall Oil (CAS no. 8002-26-4) in European Food Safety Authority site: http://www.efsa.europa.eu/, see Attachment 6 section 7 list of Annex 1.

2) See HPV task force consortium registration, www.pinechemicals.org , as part of the High Production Volume (HPV) Program. This includes summary for crude Tall Oil and Distillated Tall Oil.

10. Safety information about the substance including a Material Safety Data Sheet (MSDS) and a substance report from the National Institute of Environmental Health Studies. If the information does not exist, the petitioner should state so in the petition.

Please see enclosed the Material Safety Data Sheet of the Distillated Tall Oil by Forchem and an updated EPA report dated 9.2008 on the safety of Tall Oil and related substances.

Attachment 5, section 9: See Material Safety Data Sheet Distillated Tall Oil 20X, Forchem.

Attachment 7, section 8 : U.S. Environmental Protection Agency September 2008 Risk , Based Prioritization Document : Initial Risk-Based Prioritization of High Production Volume Chemicals , Tall Oil and related substances Category .

11. **Research information about the substance which includes comprehensive substance research reviews and research bibliographies, including reviews and bibliographies which present contrasting positions to those presented by the petitioner in supporting the substance inclusion on or removal from the national list. For Petitions to included non-organic agricultural substances onto the National list , this information item should be permitted in the production and handling of an organic product, including the availability of organic alternatives. Commercial availability does not depend upon geographic location or local market conditions. If research information does not exist for the petitioned substance, the petitioner should state so in the petition.**

There are several published reports on the use of our Tall Oil substance (CAS no. 8002-26-4) which includes crude and distilled Tall Oil. In the HPV publication, the Tall Oil relates to a variety of Tall Oil derivatives: Tall Oil, Tall Oil Pitch, Tall Oil Pitch sodium salt, Tall Oil disproportionated, Tall Oil sodium salt, Tall Oil potassium salt, Tall Oil soap acidulation and wastewater. All these substances are similar in their chemical composition, being predominantly the extractives that remain after the pulping of wood.

Tall Oil (CAS no. 8002-26-4) is known to be used as a pesticide (insecticide repellent). Recently this substance was approved by EFSA and included in the EU Annex 1 inclusion of the EU registration directive, EEC 91/414.
Tall Oil is also approved for use as emulsifier/solvent, food additive as well as in industry of plastics, fuels and lubricants.

All the following references below support that Tall Oil (CAS no. 8002-26-4) is useful and safe for our Fungicide Product as a solvent/emulsifier:

1) As Part of the High Production Volume (HPV) Program, Pine chemicals Association, Inc. has sponsored 6 HPV chemicals. The final summary (final submission to the EPA) addresses the following six chemicals, known collectively as Tall Oil Fatty Acids and Tall Oil Fatty Acid Salts, available data show that Tall Oil (CAS no. 8002-26-4) is non-toxic in acute studies and indicate that the substance is dominated by readily biodegradable compounds .

Attachment 14, section 9: High Production Volume (HPV) Chemical Challenge Program, Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. 2001.

2), As Part of the High Production Volume (HPV) Program, Pine chemicals Association, Inc. has sponsored another group of chemicals. Although our Tall Oil (CAS no .8002-26-4) is not included in this document, all mentioned Tall Oil derivates in this document are related substances to Tall Oil and are driven from or closely related to Tall Oil Fatty Acids (TOFA), a substance obtained by the fractional distillation of crude Tall Oil (CAS no. 8002-26-4), all the members of this group are similar in their chemical composition; Fatty acids Tall Oil , fatty acids Tall Oil low boiling, fatty acids unsaturated, octadecanoic acid, fatty acids Tall Oil potassium salt and fatty acids Tall Oil sodium salt. This document demonstrates that both Tall Oil Fatty Acids and monomer acids are non-toxic to fish, daphnia and algae. Tall Oil Fatty Acids (TOFA) was tested in a 90 day subchronic toxicity study in rats. The NOEL (No Observed Effect Level) was 5% (approximately 2500 mg/kg/day),

Attachment 15, section 9 : High Production Volume (HPV) Chemical Challenge Program , Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. Aug. 2004

3) In the EPA publication of September 2008 (Initial risk based prioritization of high production volume chemicals), the Tall Oil and its related substances were assessed for their environmental fate, hazard, and exposure. The information used by EPA includes data submitted under the HPV Challenge Program , the 2006 Inventory Update Reporting (IUR) and data availability through other selected sources:

Attachment 1, section 7: Initial Risk-Based Prioritization of High Production Volume Chemicals, September 2008

4) Natural oils (e.g. Tall Oil) appear to be capable of preventing water uptake by wood. A study published about Tall Oil/water –emulsions as water repellents for Scots pine sapwood. The emulsion technique is a potential method of decreasing the amount of oil needed in order to protect wood from water uptake.

Attachment 1, section 11: Anna Hyvonen et. al., Tall Oil/water –emulsions as water repellents for Scots pine sapwood, Holz als Roh-und Werkstoff (2006) 64: 68-73.

5) Tall Oil, a by-product of the Kraft process for pulping softwood, has been shown to have insecticidal properties. In the present study, the active principles in Tall Oil against the variegated cutwarm, *Peridroma sauciaa Hubner* , were investigated.

This study confirms that resin acids are major active principles in Tall Oil against the variegated cutworm, but other chemicals are also contributed to the bioactivity of Tall Oil.

Attachment 4, section 3: Yongshou Xie et. al., Diterpene resin acids: major active principles in Tall Oil against variegates cutworm,, *Peridroma saucia(*Lepidoptera, Noctuidae) Journal of Chemical Ecology, Vol. 19, No. 6, 1993.

6) Tall Oil is exempt from the requirement of a tolerance under 40 CFR 180.910 by the Environmental Protection Agency for use in pesticide formulation applied to growing crops and crops after harvest (pre-and post harvest uses).

Attachment 2, section 7: e-CFR Title 40: Protection from the Environment, exemptions from tolerances, 2.10.2008

7) Tall Oil (CAS no. 8002-26-4) is known to be used as a pesticide (insecticide repellent). Recently this substance was approved by EFSA and included in the EU Annex 1 inclusion of the EU registration directive, EEC 91/414.

Published 'Draft Assessment Report' of Tall Oil (CAS no. 8002-26-4) in European Food Safety Authority site: http://www.efsa.europa.eu/.

12. A " Petition Justification Statement " which provides justification for any of the following actions" requested in the petition:

We ,Biomor Israel Ltd., is petitioning for the inclusion of distillated Tall Oil (CAS no. 8002-26-4) in the category of organically produced agricultural products , under Section 7 CFR 205.601 (synthetic substance allowed for use in organic crop production).

The NOP defines "synthetic " as a substance that is formulated or manufactured by a chemical process or by a process that chemically changes, a substance extracted from naturally occurring plant, animal or mineral sources, except that such term shall not apply to substances created by naturally occurring biological processes.

There are several published reports on the use of our Tall Oil substance (CAS no. 8002-26-4) which includes crude and distilled Tall Oil. In the HPV publication, the Tall Oil relates to a variety of Tall Oil derivatives: Tall Oil, Tall Oil Pitch, Tall Oil Pitch sodium salt ,Tall Oil disproportionated, Tall Oil sodium salt, Tall Oil potassium salt, Tall Oil soap acidulation and wastewater. All these substances are similar in their chemical composition, being predominantly the extractives that remain after the pulping of wood.

Suitability to Organic Agriculture

We, Biomor Israel Ltd. are a young company specializing in the development and production of innovated plant protection products based on natural organic plant extracts.

Our product, *Timorex Gold,* is a propriety bio organic fungicide which is based on Tea Tree Oil (essential oil extract of the *melaleua alternifolia* plant), has proved to be highly effective against a wide rang of plant pathogens in many crops with the advantage of being an environmental friendly product for organic and conventional agriculture, thus an alternative for substituting synthetic products as well a natural product for resistant management programs.

Advantages of our product:

- Effective wide range natural, bio-organic fungicide
- No residues
- No PHI and MRL limitations
- Safe to beneficial insects and bees
- Safe to the environment
- Substitutes Copper and Sulphur compounds and other conventional fungicides.
- Tool for Resistance Management
- Organic Certified
- No stains on the crop

Benefits of Distillated Tall Oil (CAS no. 8002-26-4)

Our product 'Timorex Gold' contains in its formulation the petitioned substance Distillated Tall Oil, (CAS no. 8002-26-4).

Timorex Gold is applied by the common agriculture practice of water spray volume. For this purpose, it is essential for the formulation of our product to contain an emulsifier/solvent, thus enabling the active ingredient (the Tea Tree Oil) to mix well in the water of the spray volume.

We have tested several substances and found the Distillated Tall Oil (CAS No. 8002-26-4) to be the most appropriate substance to enhance the biological activity of our Timorex Gold product.

We urge the USDA to support the use of the Distillated Tall Oil (CAS no. 8002-26-4) for our natural bio-organic fungicide because of it's following advantages:

It is safe to use and provide excellent support to pesticide active ingredients (as solvent /emulsifier).

1. It is safe to humans because of very low toxicity.

2. It is safe to use in consumer products such as food additive.

3. It is considered to be safe to mammals because of low toxicity.

4. It is a natural product, it is readily biodegradable compound.

5. It is safe to fish and wildlife due to low toxicity to aquatic organisms

   Attachment 1, section 7: Initial Risk-Based Prioritization of High Production Volume Chemicals, EPA, September 2008

6. It is safe to consumers as the EPA has granted the **tolerance exemption** to Tall Oil; 'inert ingredient used pre and post harvest ; exemptions from the requirement of a tolerance' (Tall Oil contains: Fatty acids not less than 58%, rosin acids not more than 44% , unsaponifiables not more than 8%)

Attachment 2, section 7: EPA, e-CFR Title 40: Protection from the Environment, exemptions from tolerances, 2.10.2008

7. Tall Oil is the source of almost all of the 36 substances included in the entire PCA HPV program. Tall Oil (CAS no. 8002-26-4) has been selected as the representative substance in group of 'Tall Oil and related substances' for testing for the SIDS data.

   Attachment 14 ,section 9: High Production Volume (HPV) Chemical Challenge Program , Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. 2001

8. According to discussion document, dated Nov. 2008, by the National Organic Standards Board (NOSB) Crops Committee, regarding List inerts in Pesticide formulations, it was a mention that the NOSB is requested to work in concert with the NOP and EPA to accomplish the task of amending NOP inert ingredient regulations as they pertain to the National List . One of the possible options raised in this document that the NOP suggested, was to substitute the language in the rule currently at List 4, with the new regulatory reference for 40 CFR 180.950 (the minimal risk ingredients). This list includes Soap (The water soluble sodium or potassium salts of fatty acids produced by either the saponification of fats and oil, or the neutralization of fatty acid).

   Attachment 1 , section 12, National Organic Standards Board (NOSB), Crops Committee, List 4 Inerts in Pesticide Formulations , Discussion Document, November 2008.

9. Tall oil (CAS no. 8002-26-4) is classified as a **'low risk substance'** in the new EU regulation, dated 1.9.2008, on pesticide residues '(Reg (EC) no. 396/2005)' and defined as **'No MRL required'**.

   Attachment 2 , section 12: Pesticide EU-MRLs Database , Regulation (EC) No. 396/ 2005.

   Attachment 3 , section 12; New Rules on pesticide residues in food, European Commission, September 2008.

Tall Oil Uses

Tall Oil (CAS no. 8002-26-4) is approved for use as a pesticide (insecticide, repellent). Recently this substance was approved by EFSA and included in the EU Annex 1 inclusion of the EU registration directive, EEC 91/414.
Tall Oil is also approved for use as emulsifier/solvent, food additive as well as for use in industry of plastics, fuels and lubricants.

Registrations

Timorex Gold ,of which its formulation contains Distillated Tall Oil (CAS no, 8002-26-4) is registered in the following countries ; Israel, Honduras , Nicaragua, Colombia and Mexico. It is expected to be registered shortly in Costa Rica ,Argentina , and is in it's advanced registration steps in Australia , EU, USA and several Asian countries. Our Timorex Gold product is registered for use on fresh edible vegetables, fruits and herbs for the control of a wide range of plant pathogens such as Powdery, Downy mildews, Early and Late Blights, Scabs and more.

In accordance with the Food Quality Protection Act, in 2006 the EPA completed reassessments of inert ingredients used in pesticide products to ensure that such products met human health based on safety standards.
Tall Oil is exempt from the requirement of a tolerance under 40 CFR 180.910 by the Environmental Protection Agency for use in pesticide formulation applied to growing crops and crops after harvest (pre-and post harvest uses); "Tall Oil ; Fatty acids not less than 58%, rosin acids not more than 44% , unsaponifiables not more than 8%" . The Distillated Tall Oil we use (manufactured by Forchem) is inline with these standards and therefore approved for exemption of tolerance.

With regards to above mentioned, we request the USDA to take into consideration the above cited benefits when evaluating the Tall Oil (CAS no. 8002-26-4), and approve it for inclusion on the National Organic List.

LIST OF ATTACHMENTS

Section 1

No attachments

Section 2

No attachments

Section 3

Attachment 1, section 3: Tall oil Products Forchem

Attachment 2, section 3: Product Data Sheet Tall Oil 20X Forchem

Attachment 3, section 3: Chemurgy Standard Article J. Peter Clark ,
A. Epstein and Sons International, Inc.Article Online Posting Date: December 4, 2000, cited in Abstract chemistry Kirk- Othmer Encyclopedia

Attachment 4, section 3: Yongshou Xie et. al., Diterpene resin acids: major active principles in tall oil against variegates cutworm,, *Peridroma saucia(*Lepidoptera, Noctuidae) Journal of Chemical Ecology, Vol. 19, No. 6, 1993.

Attachment 5, section 3: Arizona chemical -Product –Applications-Surfactants

Attachment 6, section 3: . Meadwestvanco Company chemical company product, product named MWV M-28B ,Distilled Tall oil and Mixed Acids Specialty Chemicals

Attachment 7, section 3: Inert Ingredients Permitted for Use in Nonfood Use Pesticide Products Last Updated January 7, 2008, UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Attachment 8, section 3: CFSAN/Office of Food Additive Safety
July 2006, Food additive status List)

Attachment 9, section 3: Regulatory information for tall oil and tall oil registration status as adjuvant in PAN

Attachment 10, section 3: Registration status of active ingredients authorized in EU, registration as a repellent

Section 4

No Attachments

Section 5

Attachment 1, section 5: process, Wikipedia
Attachment 2, section 5: Tall oil Life Cycle (Forchem)

Attachment 3, section 5: Fractionation of the tall oil (Forchem)-for crude tall oil

Attachment 4, section 5: Fractionation of Crude tall oil (Forchem)-description letter provided by Quality Manager of Forchem Tall Oil Refinery in Rauma, Finland.

Attachment 5, section 5: Production chain Forchem for crude tall oil;

Attachment 6, section 5: Full tall oil scheme of the technological process (manufacturing process in Finnish);

Attachment 7, section 5: Figure 1-Tall oil Process Forestry Tall Oil

Section 6

No Attachments

Section 7

Attachment 1, section 7: Initial Risk-Based Prioritization of High Production Volume Chemicals, EPA, September 2008

Attachment 2, section 7: e-CFR Title 40: Protection from the Environment, exemptions from tolerances, 2.10.2008

Attachment 3, section 7: Methyl Esters of Tall-Oil Fatty Acids; Tolerance Exemption EPA 40 CFR Part 18

Attachment 4, section 7: list 3 of inert ingredients in the EPA

Attachment 5, section 7: Food additive status list

Attachment 6, section 7: Europe; existing active substances; SANCO DOC 3010

Attachment 7, section 7: Agency Response letter GRAS Notice No GRN 00039

Attachment 8, section 7: Application A417-Tall oil non-esterified phytosteols derived from tall oil, Full assessment, 10 October 2001

Attachment 9, section 7 includes the following references:

- Substances in Cosmetics and Personal Care Products regulated under the Food and Drugs Act (F& DA) .
- PMRA Consolidated list formulants sorted by CAS Number.
- U.S. Environmental Protection Agency, List of inert Pesticide Ingredients.
- PAN Pesticide Database – Pesticide Registration Status

Section 8

Attachment 1, section 8: High Production Information System (HPVIS): about reference Final Submission Information for Tall Oil and Related Substances Zinkel, D.F. and Russell, J., Eds. 1989. Naval Stores Production, Chemistry, Utilization. Pulp Chemicals Association, New York.).

Attachment 2, section 8: Label of Timorex Gold

Attachment 3, section 8: Pine Chemical Association, Atlanta: High Production Volume Chemical Challenge Program, Test Plan for Tall Oil and Related Substances, Submitted to US EPA

Section 9

Attachment 1, section 9**:** Attachment 1, section 9: Forchem Product Data sheet
Attachment 2, section 9: Koski, Anna, Applicability of crude tall oil for wood protection Faculty of Technology, Department of Process and Environmental Engineering, University of Oulu, University of Oulu, Finland ,Acta Univ. Oul. C 293, 2008

Attachment 3, section 9: Method of analysis of Tall oil Product, Journal of the American Oil Chemists Society, Volume 36,Number 3/March 1959

Attachment 4, section 9: Dybdahl, H.P. 1993. Determination of log P_{ow} for single components in tall oil pitch.

Attachment 5**,** section 9: Safety Data Sheet Distilled Tal oil 20X,Forchem

Attachment 6, section 9: Zinkel and Russell 1989, Attachment 1, section 8 and Naval Stores Research at the Forest Products Laboratory, Attachment 7, section 9: Tall Oil, Lars-Hugo Norlin, Bergvik Kemi, Sandarne, Sweden, 2005

Attachment 8, section 9: Gas chromatographic analysis of tall oil fractionation products after methylation with N,N- dimethylformamide dimethylacetal , McGuire J.M,Powis P.J.,Journal of chromatographic science 1998,vol 36,no.2,pp.104-108

Attachment 9, section 9: Al Wong,Arbokem Ink.,Vancouver,Canada,Cellulose Chemistry and Attachment 4, section 9: Al Wong,Arbokem Ink.,Vancouver,Canada,Cellulose Chemistry and Technology,36:388-37-88(2002):Degradation of crude tall oil held under heated conditions, Part1 Basic reactions and mixtures of model compounds Al Wong,Arbocem Ink.,Vancouver,Canada ,Forest Chemicals Review,113(2):12-16,2003)

Attachment 10, section 9: Wong,Arbocem Ink.,Vancouver,Canada , Basic reactions and mixtures of model compounds Al ,Part 2 :Ternary mixture of model compounds and prediction of acid number decrease, Forest Chemicals Review,113(3):11-14,2003),

Attachment11,section 9 : Gerard R.Millet and Norman S.Thomson ,The reaction of tall oil Fatty Acids , the Institute of Paper Chemistry, Appleton, WISCONSIN, may, 1979

Attachment12,section 9 : Degradation of Tall Oil Fatty Acids by Molecular Oxygen in Alkaline Media ,The Institute of Paper Chemistry ,Gerrald R. Mittet

Attachment13, section 9: ,Charlie Scrimgeour, Scottish Crop Research Institute, Dundee,Scotland,Chemistry of Fatty Acids

Attachment 14 ,section 9: High Production Volume (HPV) Chemical Challenge Program , Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. 2001

Attachment 15 ,section 9 : High Production Volume (HPV) Chemical Challenge Program , Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. Aug. 2004

References cited but not submitted:

Duncan DP (1989) Tall oil fatty acids. In: Zinkel DF & Russel J (eds) Naval stores: Production, chemistry and utilization. Pulp Chemical Association, New York, US: 346-439.

Soltes EJ & Zinkel DF (1989) Chemistry of rosin. In: Zinkel DF & Russel J (eds) Navalstores: Production, chemistry and utilization. Pulp Chemical Association, New York,
US.: 261-345.

Drew J & Propst M (1981) Tall oil: A book on the processing and use of tall oil; for

chemists, engineers, managers and producers. Pulp Chemicals Association, New York, US

Section 10

No Attachments.

Section 11

Attachment 1, section 11: Anna Hyvonen et. al., Tall oil/water –emulsions as water repellents for Scots pine sapwood, Holz als Roh-und Werkstoff (2006) 64: 68-73.

Section 12

Attachment 1 , section 12: National Organic Standards Board (NOSB), Crops Committee, List 4 Inerts in Pesticide Formulations , Discussion Document, November 2008.

Attachment 2 , section 12: Pesticide EU-MRLs Database , Regulation (EC) No. 396/ 2005.

Attachment 3 , section 12; New Rules on pesticide residues in food, European Commission.

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Section 1

No attachments

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Attachment 5, section 3: Arizona chemical -Product –Applications-Surfactants

Attachment 6, section 3: : Meadwestvanco Company chemical company product, product named MWV M-28B ,Distilled Tall oil and Mixed Acids Specialty Chemicals

Attachment 7, section 3: Inert Ingredients Permitted for Use in Nonfood Use Pesticide Products Last Updated January 7, 2008, UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Attachment 8, section 3: CFSAN/Office of Food Additive Safety
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Attachment 10, section 3: Registration status of active ingredients authorized in EU, registration as a repellent

Section 4

No Attachments

Section 5

Attachment 1, section 5: process, Wikipedia
Attachment 2, section 5: Tall oil Life Cycle (Forchem)

Attachment 3, section 5: Fractionation of the tall oil (Forchem)-for crude tall oil

Attachment 4, section 5: Fractionation of Crude tall oil (Forchem)-description letter provided by Quality Manager of Forchem Tall Oil Refinery in Rauma, Finland.

Attachment 5, section 5: Production chain Forchem for crude tall oil;

Attachment 6, section 5: Full tall oil scheme of the technological process (manufacturing process in Finnish);

Attachment 7, section 5: Figure 1-Tall oil Process Forestry Tall Oil

Section 6

No Attachments

Section 7

Attachment 1, section 7: Initial Risk-Based Prioritization of High Production Volume Chemicals, EPA, September 2008

Attachment 2, section 7: e-CFR Title 40: Protection from the Environment, exemptions from tolerances, 2.10.2008

Attachment 3, section 7: Methyl Esters of Tall-Oil Fatty Acids; Tolerance Exemption EPA 40 CFR Part 18

Attachment 4, section 7: list 3 of inert ingredients in the EPA

Attachment 5, section 7: Food additive status list

Attachment 6, section 7: Europe; existing active substances; SANCO DOC 3010

Attachment 7, section 7: Agency Response letter GRAS Notice No GRN 00039

Attachment 8, section 7: Application A417-Tall oil non-esterified phytosteols derived from tall oil, Full assessment, 10 October 2001

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- Substances in Cosmetics and Personal Care Products regulated under the Food and Drugs Act (F& DA) .
- PMRA Consolidated list formulants sorted by CAS Number.
- U.S. Environmental Protection Agency, List of inert Pesticide Ingredients.
- PAN Pesticide Database – Pesticide Registration Status

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Section 9

Attachment 1, section 9: Attachment 1, section 9: Forchem Product Data sheet
Attachment 2, section 9: Koski, Anna, Applicability of crude tall oil for wood protection Faculty of Technology, Department of Process and Environmental Engineering, University of Oulu, University of Oulu, Finland ,Acta Univ. Oul. C 293, 2008

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Attachment 4, section 9: Dybdahl, H.P. 1993. Determination of log P_{ow} for single components in tall oil pitch.

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Attachment 6, section 9: Zinkel and Russell 1989, Attachment 1, section 8 and Naval Stores Research at the Forest Products Laboratory, Attachment 7, section 9: Tall Oil, Lars-Hugo Norlin, Bergvik Kemi, Sandarne, Sweden, 2005

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Section 10

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Section 11

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Section 12

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Attachment 2 , section 12: Pesticide EU-MRLs Database , Regulation (EC) No. 396/ 2005.

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Section 1 List of Attachments

No attachments .

Section 2 List of Attachments

No attachments.

Section 3 List of Attachments

Attachment 1, section 3: Tall oil Products Forchem

Attachment 2, section 3 : Product Data Sheet Tall Oil 20X Forchem

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A. Epstein and Sons International, Inc.Article Online Posting Date: December 4, 2000, cited in Abstract chemistry Kirk- Othmer Encyclopedia

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Attachment 5, section 3: Arizona chemical -Product –Applications-Surfactants

Attachment 6, section 3: : Meadwestvanco Company chemical company product, product named MWV M-28B ,Distilled Tall oil and Mixed Acids Specialty Chemicals

Attachment 7, section 3: Inert Ingredients Permitted for Use in Nonfood Use Pesticide Products Last Updated January 7, 2008 , UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Attachment 8, section 3: CFSAN/Office of Food Additive Safety
July 2006, Food additive status List)

Attachment 9, section 3: Regulatory information for tall oil and tall oil registration status as adjuvant in PAN

Attachment 10, section 3: Registration status of active ingredients authorized in EU, registration as a repellent

Attachment 1, section 3

forchem

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- Tall Oil Fatty Acid (TOFA)
- Tall Oil Rosin (TOR)
- Distilled Tall Oil (DTO)
- Other tall oil products
- Tall Oil Life Cycle

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Visiting address.
Maanpääntie 3, 26820
RAUMA, FINLAND

Tall Oil Products

Distilled Tall Oil

DEC 15 2008

for10 is a distilled tall oil with a Rosin acid content of 10%.

for10 is an excellent raw material for different end applications such as Alkyd Resins, Soaps, Cleaners, Oilfield chemicals etc.

for20 is a distilled tall oil with a Rosin acid content of 20%.

for20 is an excellent raw material for different end applications such as Alkyd Resins, soaps, cleaners, oilfield chemicals etc.

for20x is special distilled tall oil (DTO) with the special features of fatty and rosin acids can offer

for20x is an excellent raw material to be used in metal working fluids, oil field chemicals, soaps, cleaners and alkyd resins.

for20x is specially designed from carefully selected and distilled tall oils for outmost stability and low temperature properties.

for20-25 is special distilled tall oil (DTO) with the special features of fatty and rosin acids can offer.

for20-25 is an excellent raw material to be used in metal working fluids, oil field chemicals, soaps, cleaners and alkyd resins.

for20-25x is special distilled tall oil (DTO) with the special features of fatty and rosin acids can offer

for20-25x is an excellent raw material to be used in metal working fluids, oil field chemicals, soaps, cleaners and alkyd resins.

for20-25x specially designed from carefully selected and distilled tall oils for outmost stability and low temperature properties.

for25/30 is a distilled tall oil with a rosin acid content of 25-30%.

for25/30 is an excellent raw material for production of Alkyd Resins, Metal Working Fluids, Soaps, Cleaners and Oil Field Chemicals.

for25-30x is special distilled tall oil (DTO) with the special features of fatty and rosin acids can offer

for25-30x is a excellent raw material to be used in metal working fluids,
oil field chemicals, soaps, cleaners and alkyd resins.

for25-30x is specially designed from carefully selected and distilled tall oils for outmost stability and low temperature properties.

for30-40x is special distilled tall oil (DTO) with the special features of fatty and rosin acids can offer

for30-40x is a excellent raw material to be used in metal working fluids,
oil field chemicals, soaps, cleaners and alkyd resins.

for30-40x is specially designed from carefully selected and distilled tall oils for outmost stability and low temperature properties.

HARNESSING THE POWER
OF NATURE TO ENTER
A NEW ERA IN THE
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13 th November 2008

forchem
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Product Data Sheet

DEC 5 2008

For 20x

for20x is special distilled tall oil (DTO) with the special features of fatty and rosin acids can offer.

for20x is an excellent raw material to be used in metal working fluids, oil field chemicals, soaps, cleaners and alkyd resins.

for20x is specially designed from carefully selected and distilled tall oils for outmost stability and low temperature properties.

Typical Analysis

Analysis	Typical value	Specification	Method
Acid value, mg (KOH)/1 g	192		ASTM D 465-01
Cloud point, ˚C	-1	6,5 max.	ASTM D 2500-99
Colour, Gardner (photometer)	4,5		ASTM D 6166-97
Relative Density at 20 ˚C	0,930		SCAN-T 2:65
Flash point, closed cup, ˚C	200		SCAN 6:67
Free fatty acids, %	75		ASTM D 1585-96
Free rosin acid, %	20	20±2	SCAN-T 14:78
Pour point, ˚C	-6		SCAN-T 5:67
Refractive index, n_D at 20 ˚C	1,485		SCAN-T 1:65
Saponification value	194		SCAN-T 12:72
Unsaponifiables, %	3		SCAN-T 13:74
Viscosity at 20 ˚C, cP (mPas)	80		ASTM D 2196-99

Delivery form	Deliveries in bulk by truck or ocean vessel. Liquid in road tanker, rail tank wagon, ISO-container, flexitank or 188 kgs net in steel drums.
EINECS number	232-304-6
CAS number	8002-26-4
CN-code	3803 00 90

Attachment 3, section 3

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Chemurgy

Standard Article

J. Peter Clark[1]

[1]A. Epstein and Sons International, Inc

DOI: 10.1002/0471238961.0308051303120118.a01
Article Online Posting Date: December 4, 2000

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Abstract

Chemurgy is the branch of applied chemistry concerned with the industrial use of biomass for fuel and chemicals. The biomass may be industrial crops, such as trees, cotton, or oilseeds; food crops, such as corn or soy; or wastes and by-products, such as forest trimmings, tall oil, or straw. Chemurgic processes and applications range from relatively simple physical or chemical separations, such as milling, to more sophisticated enzymatic hydrolysis of cellulose and fermentation to produce ethanol. Lignocellulosic materials, such as forest or farm wastes, can, in principle, generate most of the basic chemical building blocks now produced from oil and gas. Pyrolysis can generate oils and fuel gases to serve as alternative energy sources. The viability of chemurgic processes depends heavily on the costs of fossil fuels, considered as economic alternatives, and on the costs of biomass raw materials and the efficiencies of conversion processes.

Keywords: Chemurgy; Raw materials; Renewable resources; Industrial materials; Food crops; Wastes; By-products; Fuels; Alcohols; Textile fibers; Wood; Fermentation; Beverages; Sewage treatment

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Attachment 4, section 3

Journal of Chemical Ecology, Vol. 19, No. 6, 1993

DITERPENE RESIN ACIDS: MAJOR ACTIVE PRINCIPLES IN TALL OIL AGAINST VARIEGATED CUTWORM, *Peridroma saucia* (LEPIDOPTERA: NOCTUIDAE)

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(Received April 13, 1992; accepted January 25, 1993)

Abstract—Tall oil, a by-product of the kraft process for pulping softwood, has been shown to have insecticidal properties. In the present study, the active principles in tall oil against the variegated cutworm, *Peridroma saucia* Hübner, were investigated. GC-MS analysis showed that abietic, dehydroabietic, and isopimaric acids were major resin acid components of crude tall oil and depitched tall oil. When crude tall oil samples of differing resin acid composition were incorporated into artificial diet at a concentration of 2.0% fresh weight, they suppressed larval growth by 45–60% compared to controls. This suppression was significantly ($P \leq 0.05$) correlated with the equivalent contents of abietic, dehydroabietic, isopimaric, and total resin acids. These results were also evident from a diet choice test, showing that the second-instar larvae obviously selected diets with low levels of resin acids when different diets were randomly arranged in a Petri dish. Bioassays with pure resin acids (abietic, dehydroabietic, and isopimaric acids) demonstrated that all individual chemicals have similar bioactivity against this insect. Comparison of the bioactivities of depitched tall oil and an equivalent mixture of pure resin acids in the *Peridroma* chronic growth bioassay indicated that pure resin acids and depitched tall oil share a common mode of action to this insect. This study confirms that resin acids are major active principles in tall oil against the variegated cutworm, but other chemicals likely also contribute to the bioactivity of tall oil.

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[*] To whom correspondence should be addressed.

attachment 4, section 3

Journal of Chemical Ecology, Vol. 19, No. 6, 1993

DITERPENE RESIN ACIDS: MAJOR ACTIVE PRINCIPLES IN TALL OIL AGAINST VARIEGATED CUTWORM, *Peridroma saucia* (LEPIDOPTERA: NOCTUIDAE)

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*To whom correspondence should be addressed.

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Attachment 5 section 3

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CENTURY 1101	CENTURY® 1101 is a unique mixture of branched and straight-chain saturated C18 fatty acids. The very low level of unsaturation results in excellent thermal and oxidative stability.	🔒 MSDS 🔒 Product Data Sheet
CENTURY 1105	An isostearic acid with a unique mixture of branched and straight-chain saturated C_{18} fatty acids. The high content of branched acids makes it a liquid product, while the very low level of unsaturation results in excellent oxidative stability.	🔒 MSDS 🔒 Product Data Sheet
CENTURY 1107	A highly purified isostearic acid mixture of branched and straight-chain C_{18} fatty acids. Its high acid value is of particular value in demanding applications such as lubricant additives, personal care, and metalworking.	🔒 MSDS 🔒 Product Data Sheet
CENTURY 1224	A saturated fatty acid product containing approximately 85% C_{18} stearic acid, with typically 12% methyl-branched C_{18} saturated acids.	🔒 MSDS 🔒 Product Data Sheet
CENTURY D-1	Monomeric fatty acid distillate obtained from the dimerization reaction of tall oil fatty acid. CENTURY D-1 is a mixture of branched and straight chain fatty acids.	🔒 MSDS 🔒 Product Data Sheet
CENTURY MO-5N	A fatty acid product that contains both saturated and unsaturated C_{18} fatty acids that is used in paste soaps and detergents, and also in esters for various lubricant applications such as metalworking and textile lubricants.	🔒 MSDS 🔒 Product Data Sheet
CENTURY MO-6	CENTURY MO-6® is a fatty acid product containing both saturated & unsaturated C-18 fatty acids. It finds application in paste soaps and detergents & for esters for lubricant applications such as metalworking & textile lubricants. **Available in EU only.**	🔒 MSDS 🔒 Product Data Sheet
CENWAX G	This triglyceride of 12-hydroxystearic acid is a hard, brittle, high melting synthetic wax which is insoluble in most organic solvents.	🔒 MSDS 🔒 Product Data Sheet
SYLFAT BK	SYLFAT® BK is a tall oil fatty acid (TOFA) with a high fatty acid content. SYLFAT® BK provides a combination of light color, very good color stability and air drying properties. **Available in EU only.**	🔒 MSDS 🔒 Product Data Sheet
SYLFAT FA-1	An economical low-cost source of liquid fatty acid that is light in color and low in rosin.	🔒 MSDS 🔒 Product Data Sheet
SYLFAT FA-1 Special	A special SYLFAT TOFA grade designed to meet a broad range or applications due to its high acid number, lower rosin and lighter color compared with other TOFA grades.	🔒 MSDS 🔒 Product Data Sheet
SYLFAT FA-2	A SYLFAT TOFA grade designed to meet a broad range or applications due to its high acid number, lower rosin and lighter	🔒 MSDS

	color compared with other TOFA grades.	Product Data Sheet
SYLVAPINE 401	SYLVAPINE® 401 is a blend of SYLVAPINE® 402 alpha-pinene and SYLVAPINE® 405 dipentene. **Available in EU only.**	MSDS Product Data Sheet
SYLVAPINE 402	An alpha-pinene used as an intermediate for making camphor, perfumes, terpineol, resins and insecticides. SYLVAPINE 402 can also be used as a cleaner, solvent and a disinfectant. **Available in EU only.**	MSDS Product Data Sheet
SYLVAPINE 402 SF	A sulphur free alpha-pinene used as an intermediate for making camphor, perfumes, terpineol, resins and insecticides. It can also be used as a cleaner, solvent and a disinfectant. **Available in EU only.**	MSDS Product Data Sheet
SYLVAPINE A ALPHA-PINENE	A clear, colorless liquid with a mild turpentine-like odor that is very high in alpha-pinene content. It is miscible in alcohols and insoluble in water.	MSDS Product Data Sheet
SYLVAROS 331GP/55	SYLVAROS® 331GP/55 can be used as a polymerization emulsifier for making synthetic rubbers. **Available in EU only.**	MSDS Product Data Sheet
SYLVAROS 356/85	SYLVAROS® 356/85 is a potassium soap of disproportionated tall oil rosin. **Available in EU only.**	MSDS Product Data Sheet
SYLVAROS 356/NA	SYLVAROS® 356NA is a disproportionated tall oil rosin, which is hardened by sodium hydroxide. It can be used as polymerization emulsifier for making synthetic rubber. **Available in EU only.**	MSDS Product Data Sheet
SYLVAROS 90	SYLVAROS® 90 is a high quality tall oil rosin (TOR), characterized by high rosin acid content, pale color and good color stability. SYLVAROS® 90 is an excellent starting material for the manufacture of various rosin derivatives. **Available in EU only.**	MSDS Product Data Sheet
SYLVATAL 10S	SYLVATAL® 10S, a distilled tall oil (DTO), combines the advantages of fatty and rosin acids. It is suitable raw material for metal working fluids, oil field chemicals, soaps, cleaners and alkyd resins. **Available in EU only.**	MSDS Product Data Sheet
SYLVATAL 15S	SYLVATAL® 15S, a distilled tall oil (DTO), combines the advantages of fatty and rosin acids. It is therefore a suitable raw material for metal working fluids, oil field chemicals, soaps, cleaners and alkyd resins. **Available in EU only.**	MSDS Product Data Sheet
SYLVATAL 20S	SYLVATAL® 20S, a plant specific distilled tall oil (DTO), combines the advantages of fatty and rosin acids. It is therefore a suitable raw material for metal working fluids, oil field chemicals, soaps, cleaners and alkyd resins. **Available in EU only.**	MSDS Product Data Sheet
SYLVATAL 25/30NL	SYLVATAL® 25/30NL, a special distilled tall oil (DTO), combines the advantages of fatty and rosin acids. It is therefore a suitable raw material for metal working fluids, oil field chemicals, soaps, cleaners and alkyd resins. **Available in EU only.**	MSDS Product Data Sheet
SYLVATAL 25/30S	SYLVATAL® 25/30S, a plant specific distilled tall oil (DTO), combines the advantages of fatty and rosin acids. It is therefore a suitable raw material for metal working fluids, oil field chemicals, soaps, cleaners and alkyd resins. **Available in EU only.**	MSDS Product Data Sheet
SYLVATAL D40LR	A source of tall oil fatty acid having a high tall oil rosins content.	MSDS Product Data Sheet
SYLVATAL S40	A source of tall oil fatty acid having a high tall oil rosin content.	MSDS Product Data Sheet
UNIDYME 18	A low monomer content Dimer Acid specifically designed for ink and hot melt adhesive polyamides. Applications for its use also include synthetic lubricants, corrosion inhibitors and alkyd resins.	MSDS Product Data Sheet

UNIDYME 22	A Dimer Acid designed for use in lower viscosity resins such as polyamide curing agents, polyesters, and alkyds. This dimmer is also used in corrosion inhibition for oil field, refinery process, lubricant and fuel applications.	**MSDS** **Product Data Sheet**
UNIDYME M-35	UNIDYME M-35 dimer acid is a dimerized fatty acid composed of dicarboxylic and tricarboxylic acids. Its carboxylic groups and double-bond unsaturation undergo many chemical reactions to form a wide variety of chemical intermediates.	**MSDS** **Product Data Sheet**

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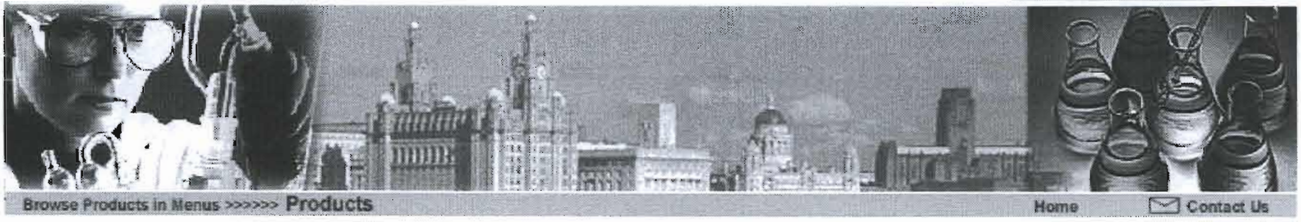

TALL OIL

- Sylfat 5
- Sylfat 2
- Sylfat 2 LT
- Sylvatal 25/30N Light
- Sylvatal 25/30S
- Sylvatal 20/25
- Sylvatal 10S

Thank you for Visiting MKR

TALL OIL PRODUCT APPLICATIONS

SYLFAT: is a tall oil fatty acid (TOFA) with high fatty acid content and a low content of resin acids and unsaponifiables. Sylfat provides a combination of light colour, very good colour stability and air drying properties.

APPLICATIONS: Sylfat products have a partially unsaturated C18 backbone and are used in wide range of applications including alkyd resins, dimer acids, surfactants, cleaners, oil field chemicals, lubricant esters and other chemical derivatives.

SYKVATAL: products are distilled tall oils (DTO), with 10-30% resin acids. They combine the advantages of fatty- and resin acids and are therefore and ideal raw material for functional products like metalworking flids, oil field chemicals, soaps, cleaners and alkyd resins. Varnishes for indoor use based on DTO use have hard films, with high gloss and excellent water and alkali resistance. Magnesium soaps of DTO are very efficient dispersants for fuel oils.

Products

Oleochemicals

-Fatty Acids
-Fatty Alcohols
-Glycerine
-Castor Oils
-Tall Oil Products

Waxes

-Paraffin Waxes
-Microcrystalline Waxes
-SMDS Waxes
-Polyethylene Waxes
-Montan Waxes
-Waxes for Cosmetics

Soap Bases

Slack Waxes

Base Oils

Epoxy Resins

Petroleum Jellies

White Oil

Asphaltum

Lard Oil/Neatfoot Oil

Alkanolamides

Ethylene BisStearamide

Attachment 6, section 3

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Distilled Tall Oil and Mixed Acids

Our tall oil chemicals are also used as emulsifiers in the polymerization of synthetic rubber and extended SBR latex, metalworking oils, alkyd resins, anionic flotation reagents and asphalt emulsion additives. These products include distilled tall oils and stabilized mixed acids.

Product Options

Distilled Tall Oils

- **MWV M-15**
  This medium-colored tall oil distillate, which contains fatty acids and approximately 15 percent rosin, is used in metalworking compounds, alkyd resins and pine oil cleaners.
- **MWV M-28B**
  This medium-colored tall oil distillate contains fatty acids and approximately 30 percent rosin. It offers improved quality in fatty acid applications where rosin content and light color are important. It is used as an emulsifier for oil extended SBR latex and for metalworking oils, as a base for alkyd resins, as an anionic flotation reagent, to formulate pine oil cleaners and as an asphalt emulsion additive.
- **MWV M-38**
  This medium-colored tall oil distillate, which contains fatty acids and approximately 40 percent rosin, is used in metalworking formulations and in other applications requiring a high rosin content mixed acid.

Stabilized Mixed Acids

- **MWV M-30D, MWV M-40, MWV M-70**
  These products are blends of catalytically stabilized tall oil rosin and fatty acids. They are used primarily as emulsifiers in the polymerization of styrene and butadiene for synthetic rubber and in other applications requiring a blend of catalytically stabilized fatty acids and rosin acids.

  M-30 contains approximately 30 percent stabilized rosin; M-40 contains 40 percent stabilized rosin; M-70 contains 70 percent stabilized rosin.

Product uses

Synthetic Rubber
Emulsifiers
SBR Latex
- Emulsifiers
- Metalworking Oils
- Alkyd Resins

Asphalt Emulsion
- Additives

Meets the needs of these industries

Industrial & Automotive

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MWV Specialty Chemicals General Information: +1 (800) 458-4034 or (843) 740-2236
Customer Service: +1 (800) 821-7345 or (800) 348-6323
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Attachment 7, section 3

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

Inert Ingredients Permitted for Use in Nonfood Use Pesticide Products

Last Updated January 7, 2008

DEC 15 2008

The following inert ingredients are permitted for use in nonfood use pesticide products.

NOTE: All inert ingredients as described in 40 CFR Part 180 may also be used in nonfood use pesticide products.

CAS Reg. No.	Chemical Name
100-02-7	p-Nitrophenol
100092-50-0	Sodium dodecylphenyl polyoxyethylene phosphates
10016-20-3	α-Cyclodextrin
10024-97-2	Nitrous oxide (N2O)
10025-67-9	Sulfur chloride (S2Cl2)
10025-74-8	Dysprosium chloride (DyCl3)
10025-76-0	Europium chloride (EuCl3)
10025-77-1	Ferric chloride
10025-94-2	Yttrium chloride (YCl3), hexahydrate
1002-62-6	Decanoic acid, sodium salt
10028-21-4	Sulfuric acid, iron(2+) salt (1:1), dihydrate
10028-22-5	Ferric sulfate
1002-89-7	Octadecanoic acid, ammonium salt
10031-30-8	Tricalcium phosphate (Ca3(PO4)2)
10034-76-1	Calcium sulfate hemihydrate
10034-85-2	Hydriodic acid
10034-88-5	Sodium bisulfate monohydrate
10034-99-8	Magnesium sulfate heptahydrate
10035-04-8	Calcium chloride
10035-10-6	Hydrobromic acid
100-37-8	2-(Diethylamino)ethanol
100403-38-1	Glycerides, animal, reaction products with sucrose
100403-39-2	Glycerides, palm-oil, reaction products with sucrose
100403-40-5	Glycerides, tallow, reaction products with sucrose
100403-41-6	Glycerides, vegetable-oil, reaction products with sucrose
100-41-4	Ethylbenzene

Attachmt 7, section 3
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CAS Reg. No.	Chemical Name
100-42-5	Styrene
10043-01-3	Aluminum sulfate
10043-35-3	Boric acid
10043-52-4	Calcium chloride (CaCl2)
10043-67-1	Potassium aluminum sulfate
10043-83-1	Magnesium phosphate
10045-89-3	Ferrous ammonium sulfate
10049-04-4	Chlorine dioxide
100-51-6	Benzyl alcohol
100-52-7	Benzaldehyde
10058-23-8	Monopotassium peroxymonosulfate
100-66-3	Benzene, methoxy-
100684-20-6	Fatty acids, tall-oil, maleated, compds. with triethanolamine
100852-66-2	Citric acid, bis(dimethylamine) salt
1008-72-6	Benzenesulfonic acid, 2-formyl-, sodium salt
100934-04-1	2-Propenoic acid, 2-methyl-, polymer with methyl 2-methyl-2-propenoate and alpha-(2-methyl-1-oxo-2-propenyl)-omega-methoxypoly(oxy-1,2-ethanediyl)
10094-34-5	Butanoic acid, 1,1-dimethyl-2-phenylethyl ester
10094-62-9	D-Glycero-D-gulo-heptonic acid, sodium salt, dihydrate
100-97-0	Hexamethylenetetramine
10099-58-8	Lanthanum chloride
10101-39-0	Silicic acid (H2SiO3), calcium salt (1:1)
10101-41-4	Calcium sulfate dihydrate
10101-50-5	Sodium permanganate
10101-66-3	Diphosphoric acid, ammonium manganese(3+) salt (1:1:1)
101-02-0	Dehydrated castor oil-maleic anhydride adduct
10102-17-7	Thiosulfuric acid (H2S2O3), disodium salt, pentahydrate
10102-18-8	Sodium selenite
10102-40-6	Molybdic acid (H2MoO4), disodium salt, dihydrate
10103-46-5	Calcium phosphate
10107-99-0	Diethylene glycol abietate
10108-91-5	Dimethylditetradecylammonium chloride
10117-38-1	Potassium sulfite
10124-31-9	Ammonium phosphate
10124-41-1	Calcium thiosulfate
10124-43-3	Cobalt sulfate
10124-56-8	Sodium polymetaphosphate
10124-65-9	Dodecanoic acid, potassium salt
101-25-7	N,N'-Dinitrosopentamethylenetetramine
10137-74-3	Calcium chlorate
10138-04-2	Ferric ammonium sulfate
10143-60-9	Di(2-ethylhexyl)ether
101-86-0	alpha-Hexylcinnamaldehyde
10191-41-0	dl-α-Tocopherol
10192-30-0	Ammonium bisulfite

CAS Reg. No.	Chemical Name
1318-00-9	Vermiculite
1318-02-1	Zeolites (excluding erionite (CAS Reg. No. 66733-21-9))
1318-23-6	Boehmite (Al(OH)O)
1318-74-7	Kaolinite (Al2(OH)4(Si2O5))
1318-93-0	Montmorillonite
1319-77-3	Cresol
1320-06-5	2-Naphthalenol, 1-{{4-{(dimethylphenyl)azo}dimethylphenyl}azo}-
1320-07-6	Benzenesulfonic acid, 4-{{3-{(dimethylphenyl)azo}-2,4-dihydroxyphenyl}azo}-, monosodium salt
1320-37-2	Dichlorotetrafluoroethane
1321-69-3	Naphthalenesulfonic acid, sodium salt
1321-74-0	Divinyl benzene
132175-04-3	Polyethylene glycol-polyisobutenyl anhydride-tall oil fatty acid copolymer (minimum number averag
132-27-4	Sodium 2-phenylphenate
1322-93-6	Sodium diisopropylnaphthalene sulfonate
1322-98-1	Sodium decylbenzene sulfonate
1323-19-9	Sodium triisopropylnaphthalene sulfonate
1323-38-2	9-Octadecenoic acid, 12-hydroxy-, (9Z,12R)-, monoester with 1,2,3-propanetriol
13235-36-4	Glycine, N,N'-1,2-ethanediylbis[N-(carboxymethyl)-, tetrasodium salt, tetrahydrate
1323-83-7	Glyceryl distearate
132-43-4	Taurine, N-cyclohexyl-N-palmitoyl-, sodium salt
132538-94-4	Oils, orange-juice, citrus sinensis
13254-34-7	2-Heptanol, 2,6-dimethyl-
132580-45-1	Alpha-{2,4,6-Tris{1-(phenyl)ethyl}phenyl}-omega-hydroxypoly(oxyethylene)poly(oxypropylene)copolym
132647-09-7	Fatty acids, coco, reaction products with 2-{(2-aminoethyl)amino}ethanol, bis(2-carboxyethyl)deri
1327-36-2	Aluminatesilicate
1327-41-9	Aluminum chloride, basic
1327-43-1	Silicic acid, aluminum magnesium salt
1327-44-2	Potassium aluminum silicate, anhydrous
132778-08-6	D-Glucopyranose, oligomeric, C9-11-alkyl glycosides
1328-53-6	C.I. Pigment Green 7
1330-20-7	Xylene
1330-38-7	Copper, (dihydrogen phthalocyaninedisulfonato(2-)), disodium salt
1330-43-4	Boron sodium oxide (B4Na2O7)
133-07-3	N-(Trichloromethylthio)phthalamide
1330-76-3	Dioctyl-2-butenedioate
1330-80-9	Propylene glycol monooleate
1331-61-9	Dodecylbenzenesulfonic acid, ammonium salt
1332-09-8	Pumice
1332-37-2	Iron oxide

CAS Reg. No.	Chemical Name
139-08-2	N,N-Dimethyl-N-tetradecylbenzenemethaneaminium chloride
139-13-9	Aminotriethanoic acid
139168-80-2	Fatty acids, tall oil,polymers with bisphenol A, epichlorohydrin, ethylene-manuf.-by-product di
139-44-6	Glyceryl tris(12-hydroxystearate)
13961-86-9	Diethanolamine oleate
13983-17-0	Wollastonite (Ca(SiO3))
13983-17-0	Soapbark (Quillaja saponin)
13986-24-8	Sulfuric acid, zinc salt (1:1), hexahydrate
139871-83-3	2-Butenedioic acid (Z)-, polymer with ethenol and ethenyl acetate, sodium salt
139-87-7	Ethyl diethanolamine
139-88-8	Sodium tetradecyl sulfate
139895-03-7	Diethoxylated methyl .alpha.-glucopyranoside 2,6-dioleate
139-89-9	Trisodium (2-hydroxyethyl)ethylenediaminetriacetate
139-96-8	Triethanolamine lauryl sulfate
140-01-2	Pentasodium diethylenetriaminepentaacetate
140-11-4	Benzyl acetate
1401-55-4	Tannic acid
14025-15-1	Ethylenediaminetetraacetic acid (EDTA), disodium copper(II) salt
14025-21-9	Potassium 3-(2-(2-((2-(2-hydroxyethyl)ethyl)octadecylamino)ethoxy)propionate
14038-43-8	C.I. Blue Pigment 27
1406-18-4	Vitamin E
140-66-9	4-(1,1,3,3-Tetramethylbutyl)phenol
140-95-4	N,N'-bis(Hydroxymethyl)urea
141-04-8	Diisobutyl adipate
141-22-0	9-Octadecenoic acid, 12-hydroxy-, (9Z,12R)-
141-32-2	Butyl acrylate
141370-38-9	2-Propenoic acid, polymer with ethenylbenzene and 2-methyl-2-[(1-oxo-2-propenyl}amino]-1-propanesulfonic acid, sodium salt
141-43-5	Ethanol, 2-amino-
141-53-7	Sodium formate
1415-93-6	Humic acids
14167-87-4	Decyl diphenyl phosphate
14168-73-1	Sulfuric acid magnesium salt (1:1), monohydrate
141754-64-5	2-Propenoic acid, telomer with 2-propanol, ammonium salt
141-78-6	Ethyl acetate
141-79-7	Mesityl oxide
141-97-9	Butanoic acid, 3-oxo-, ethyl ester
142-03-0	Aluminum acetate, basic
142-15-4	Sodium isethionate, oleic acid ester
142-17-6	9-Octadecenoic acid (9Z)-, calcium salt
142-18-7	Dodecanoic acid, 2, 3-dihydroxypropyl ester
142-31-4	Sodium octyl sulfate
14233-37-5	C.I. Solvent Blue 36

CAS Reg. No.	Chemical Name
21245-02-3	4-(Dimethylamino)benzoic acid, 2-ethylhexyl ester
212842-88-1	1,3 benzene dicarboxylic acid, 5-sulfo-, 1,3-dimethyl ester, sodium salt, polymer with 1,3-benzene dicarboxylic acid, 1,4-benzene dicarboxylic acid, dimethyl 1,4-benzene dicarboxylate and 1,2-ethanediol
21564-17-0	2-(Thiocyanomethylthio)benzothiazole
215731-95-6	2,5-Furandione, polymer with alpha-ethenyl-omega-hydroxypoly(oxy-1,2-ethanediyl), sodium salt
2163-42-0	2-Methyl-1,3-propanediol
21645-51-2	Aluminum hydroxide (Al(OH)3)
21652-27-7	2-[(Z)-8-Heptadecenyl]-2-imidazoline-1-ethanol
21662-09-9	4-Decenal, (4Z)-
219714-96-2	Penoxsulam
22047-49-0	Octadecanoic acid, 2-ethylhexyl ester
2211-98-5	Sodium p-dodecylbenzenesulfonate
2211-99-6	Benzenesulfonic acid, 4-(1 -methylundecyl)-, sodium salt
2212-50-2	Benzenesulfonic acid, 4-(1 -ethyldecyl)-, sodium salt
2212-51-3	Benzenesulfonic acid, 4-(1 -propylnonyl)-, sodium salt
2212-52-4	Benzenesulfonic acid, 4-(1 -pentylheptyl)-, sodium salt
221667-31-8	Cyprosulfamide (approval pending do not use)
222716-38-3	Fatty acids, tall-oil, esters with polyethylene glycol mono(hydrogen maleate), compds. with amides from diethylenetriamine and tall-oil fatty acids
222716-82-7	Siloxanes and silicones, di-Me, hydroxy Me, ethers with polypropylene glycol mono-Bu ether
2235-54-3	Ammonium dodecyl sulfate
2244-21-5	Troclosene potassium [USAN:INN]
22464-99-9	2-Ethylhexanoic acid, zirconium salt
225234-12-8	Borage seed oil
22620-93-5	Decanoic acid, aluminum salt
22691-02-7	Calcium chloride (CaCl2), hydrate
2269-22-9	2-Butanol, aluminum salt
23089-26-1	3-Cyclohexene-1-methanol,α,4-dimethyl-α-(4-methyl-3-pentenyl)-, {S-(R*,R*)}-
2321-07-5	Spiro(isobenzofuran-1(3H), 9'-(9H)xanthen)-3-one, 3',6'-dihydroxy-
23328-53-2	Phenol, 2-(2H-benzotriazol-2-yl)-6-dodecyl-4-methyl-
23386-52-9	Butanedioic acid, sulfo-, 1,4-dicyclohexyl ester, sodium salt
2353-45-9	FD&C Green No. 3
23696-85-7	2-Buten-1-one, 1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-
23783-42-8	Tetraethylene glycol methyl ether
2390-60-5	C.I. Basic Blue 7
241483-16-9	Poly(oxy-1,2-ethanediyl), alpha-methyl-omega-hydroxy-, maleated, calcium salts
2425-77-6	1-Decanol, 2-hexyl-
2425-85-6	C.I. Pigment Red 3
24360-05-2	Hexamethylene tetramine monohydrochloride

CAS Reg. No.	**Chemical Name**
60840-87-1	Ethanesulfonic acid, 2-(9-octadecenylamino)-, monosodium salt, (Z)-
60864-33-7	Benzyl ether of 1,1,3,3-tetramethylbutylphenoxypolyethoxy ethanol
60874-89-7	Polyoxyethylene* methylenebis(diamylphenol) *(18 moles)
60874-90-0	Sodium isopropyl isobutyl naphthalene sulfonate
60883-84-3	Sodium methylnonylnaphthalene sulfonate
60883-89-8	Tridecylbenzenesulfonic acid, dimethylamine salt
60883-90-1	Dimethylamine propylamine tridecylbenzenesulfonate
60933-42-8	Trimethylnaphthalenesulfonic acid sodium salt
609-54-1	Benzenesulfonic acid, 2,5-dimethyl-
6100-05-6	Citric acid, tripotassium salt, monohydrate
6104-30-9	Isobutylidenediurea
6104-58-1	C.I. Acid Blue 90
6104-59-2	C.I. Acid Blue 83
6107-56-8	Calcium octanoate
61181-29-1	2-Propenoic acid, 2-methyl-, dodecyl ester, polymer with 1,2-ethanediyl bis(2-methyl-2-propenoate)
6131-90-4	Acetic acid, sodium salt, trihydrate
6132-02-1	Carbonic acid, disodium salt, decahydrate
6132-04-3	Citric acid, trisodium salt, dihydrate
614-45-9	tert-Butyl perbenzoate
6152-33-6	[1,1'-Biphenyl]-2-ol, sodium salt, tetrahydrate
61524-98-9	Polyoxyethylene* hydroabietyl alcohol *(16 moles)
6153-56-6	Ethanedioic acid, dihydrate
61693-41-2	Ethanol, 2,2'-iminobis-, compd. with hexadecyl dihydrogen phosphate
61702-73-6	1H-Imidiazolium, 1,1-bis(carboxymethyl)-4,5-dihydro-2-undecyl-, hydroxide, disodium salt
61725-89-1	Tridecyloxypoly(ethyleneoxy)* poly(propyleneoxy)**-2-propanol *(9 moles) **(3 moles)
61-73-4	3,7-Bis(dimethylamino)-phenothiazin-5-ium chloride
61757-59-3	Poly(oxy-1,2-ethanediyl), α-(carboxymethyl)-ω-(tridecyloxy)-, sodium salt
61788-44-1	Styrenated phenol
61788-47-4	Fatty acids, coco
61788-48-5	Acetylated lanolin
61788-59-8	Fatty acids, coco, Me esters
61788-60-1	Methyl esters of cottonseed oil
61788-61-2	Fatty acid esters, tallow, Me ester
61788-65-6	Fattys acids, vegetable-oil, potassium salts
61788-66-7	Fatty acids, vegetable-oil
61788-67-8	Fatty acids, vegetable-oil, sulfated, sodium salts
61788-72-5	Octyl epoxytallate
61788-85-0	Castor oil, hydrogenated, ethoxylated
61788-89-4	Fatty acids, C18-unsatd., dimers
61788-92-9	Dimethyl soya alkyl ammonium chloride
61788-93-0	Coco dimethylamine
61789-01-3	Tall oil, epoxidized, 2-ethylhexyl esters

CAS Reg. No.	Chemical Name
61789-14-8	Glycerides, tallow sesqui-, hydrogenated
61789-18-2	Coco alkyltrimethyl quaternary ammonium chlorides
61789-23-9	Fatty acids, corn-oil, potassium salts
61789-24-0	Fatty acids, corn-oil, sodium salts
61789-30-8	Fatty acids, coco, potassium salts
61789-31-9	Fatty acids, coco, sodium salts
61789-36-4	Calcium naphthenate
61789-39-7	1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-, N-coco acyl derivs., chlorides, sodium salts
61789-40-0	Cocamidopropyl betaine
61789-51-3	Cobalt naphthenate
61789-56-8	Fatty acids, peanut-oil, potassium salts
61789-57-9	Fatty acids, peanut-oil, sodium salts
61789-60-4	Coal tar
61789-65-9	Resin acids and rosin acids, aluminum salts
61789-72-8	Dimethyl benzyl hydrogenated tallow ammonium cation
61789-73-9	Dialkyl(hydrogenated tallow)benzylmethylammonium chloride
61789-75-1	Benzyldimethyl-9-octadecenylammonium chloride
61789-76-2	Cocodiamine
61789-77-3	Dialkyl* dimethyl ammonium chloride *(as in fatty acids of coconut oil)
61789-80-8	Quaternary ammonium compounds, bis(hydrogenated tallow alkyl)dimethyl, chlorides
61789-86-4	Calcium petroleum sulfonates
61789-91-1	Jojoba seed oil
61789-97-7	Tallow
61789-98-8	Cork
61789-99-9	Lard
61790-12-3	Fatty acids, tall-oil
61790-24-7	Fatty acids, soya, potassium salts
61790-25-8	Fatty acids, soya, sodium salts
61790-31-6	Amides, tallow, hydrogenated
61790-33-8	Amines, tallow alkyl
61790-37-2	Fatty acids, tallow
61790-38-3	Fatty acids, tallow, hydrogenated
61790-41-8	Quaternary ammonium compounds,trimethylsoya alkyl, chlorides
61790-47-4	Amines, rosin alkyl
61790-50-9	Potassium salt of wood rosin acids
61790-51-0	Sodium salt of hydrocarbon insoluble fraction of rosin
61790-53-2	Kieselguhr (less than !% crystalline silica)
61790-59-8	Hydrogenated tallow alkyl amine acetate
61790-63-4	Diethanolamine cocoate
61790-66-7	Fatty acids, tall-oil, compds. with diethanolamine
61790-85-0	Ethoxylated N-tallow alkyltrimethylene diamines
61790-86-1	Fatty acids, tall-oil, monoesters with sorbitan, ethoxylated
61790-88-3	Fatty acids, tall-oil, triesters with sorbitan, ethoxylated

CAS Reg. No.	Chemical Name
61790-90-7	Polyoxyethylene* sorbitol hexa tall oil ester *(40 moles)
61790-92-9	Polyoxyethylene* sorbitol penta tall oil ester *(40 moles)
61791-00-2	Polyethylene glycol ester of tall oil fatty acids
61791-01-3	Fatty acids, tall-oil, diesters with polyethylene glycol
61791-06-8	Polyethylene glycol sesquiester of tallow acids
61791-07-9	Fatty acids, soya, ethoxylated
61791-08-0	Polyoxyethylene* monoethanolamide of coconut oil fatty acids *(2 moles)
61791-10-4	Quaternary ammonium compounds, coco alkylbis(hydroxyethyl)methyl, ethoxylated, chlorides
61791-12-6	Castor oil, ethoxylated
61791-14-8	Amines, cocoakyl, ethoxylated
61791-23-9	Soybean oil, ethoxylated
61791-24-0	Amines, soya alkyl, ethoxylated
61791-26-2	Polyoxyethylene* tallow amine *(20 moles)
61791-28-4	Alcohols, tallow, ethoxylated
61791-29-5	Fatty acids, coco, ethoxylated
61791-31-9	N,N-Bis(2-hydroxyethyl)(coconut oil alkyl)amine
61791-34-2	Onium compounds, morpholinium, 4-ethyl-4-soya alkyl, Et sulfates
61791-41-1	Sodium N-methyl-N-(tall-oil alkyl) taurate
61791-44-4	Alkyl* N,N-bis(2-hydroxyethyl)amine *(100% C12-C18)
61791-47-7	Bis(2-hydroxyethyl) cocoamine oxide
61791-48-8	Fatty acid, tall-oil, monoesters with sorbitan
61791-53-5	N-Tallow alkyltrimethylenediamines, oleates
61791-56-8	.beta.-Alanine, N-(2-carboxyethyl)-, N-tallow alkyl derivs., disodium salts
61791-59-1	Glycine, N-methyl-, N-coco acyl derivs., sodium salts
61792-31-2	Dodecanamide, N-[3-(dimethyloxidoamino) propyl]-
617-97-0	Benzenesulfonic acid, 3-methyl-
61814-79-7	C.I. Direct Blue 189
61824-34-8	Poly(oxy-1,2-ethanediyl), . alpha.-hydro-ω-hydroxy-, ether with D-glucitol (1:1), penta-9-octadecenoate, (all-Z)-
61827-84-7	(Octyloxy) poly(oxyethylene) poly(oxypropylene)
61847-48-1	Benzoic acid, 4-{{(2,5-dichlorophenyl)amino}carbonyl}-2-{{2-hydroxy-3-{{(2-methoxyphenyl)amino}carbonyl}-1-naphthalenyl}azo}-, methyl ester
61849-72-7	Polypropylene glycol beta-methyl glucoside ether (4:1)
61916-40-3	Disodium cupric ethylenediaminetetraacetate
61931-75-7	Benzenesulfonic acid, undecyl-, ammonium salt
6197-30-4	2-Ethylhexyl 2-cyano-3,3-diphenylacrylate
62073-57-8	Urea, N,N'bis(hydroxymethyl)-, polymer with formaldehyde and (hydroxymethyl)urea
62147-77-7	Poly(oxy-1,2-ethanediyl), α, α'-{{{4-{(2,5-disulfophenyl)azo}phenyl}imino}di-2,1-ethanediyl}bis{ω-hydroxy-, disodium salt
6227-14-1	C.I. Direct Violet 9, disodium salt
62-33-9	Calcium disodium ethylenediaminetetraacetate
62386-95-2	Methyl vinyl ether-maleic acid copolymer calcium sodium salt,minimum numb

CAS Reg. No.	Chemical Name
64742-55-8	Distillates (petroleum), hydrotreated light paraffinic
64742-56-9	Distillate (petroleum), solvent dewaxed light paraffinic distillate
64742-65-0	Distillates (petroleum), solvent-dewaxed heavy paraffinic
64742-69-4	Petrolatum
64742-81-0	Kerosene (petroleum) hydrodesulfurized
64742-88-7	Solvent naphtha (petroleum), medium aliphatic
64742-89-8	Solvent naphtha (petroleum), light aliph.
64742-94-5	Heavy aromatic solvent naphtha (petroleum)
64742-95-6	Solvent naphtha (petroleum), light aromatic
64742-96-7	Solvent naphtha (petroleum), heavy aliphatic
64743-02-8	Alkenes, α-
64754-90-1	Chlorinated polyethylene
64754-97-8	Fatty acids, coco, calcium salts
64755-04-0	Hydroxylated aminoethylamide
64755-05-1	Quaternary ammonium compounds, bis(hydroxyethyl)methyltallow alkyl, ethoxylated, chlorides
64771-72-8	Paraffins (petroleum), normal C5-20
6484-52-2	Ammonium nitrate
6485-40-1	2-Cyclohexen-1-one,2-methyl-5-(1-methylethenyl)-,(5R)-
64-86-8	Colchicine
6487-39-4	Lanthanum carbonate octahydrate (La2(CO3)3.8H2O)
65071-95-6	Polyoxyethylene tall-oil (Mol. Wt. 700-5000)
65072-00-6	Caseins, hydrolyzates
65087-00-5	1,3-Benzenediol, 2,4-bis[(4-dodecylphenyl)azo]-
65122-06-7	C.I. Basic Red 14 acetate
65138-84-3	1-Hexadecanol, dihydrogen phosphate, compd. with diethanolamine (1:2)
65143-89-7	Disodium hexadecyldiphenyloxide disulfonate
65212-77-3	C.I. Pigment Yellow 183
65-23-6	3,4-Pyridinedimethanol, 5-hydroxy-6-methyl-
6528-34-3	Butanamide, 2-[(4-methoxy-2-nitrophenyl)azo]-N-(2-methoxyphenyl}-3-oxo-
65330-59-8	1,2,3-propanetricarboxylic acid, 2-hydroxy-, copper(2+) sodium salt (1:1:2)
65381-09-1	Decanoic acid, ester with 1,2,3-propanetriol octanoate
65392-81-6	Xanthylium, 9-(2,4-dicarboxyphenyl)-3,6-bis(diethylamino)-, hydroxide, inner salt, sodium salt
65405-40-5	2-Propenoic acid, 2-methyl-, dodecyl ester, polymer with hexadecyl 2-methyl-2-propenoate, octadecyl 2-methyl-2-propenoate and tetradecyl 2-methyl-2-propenoate
6542-37-6	1H,3H,5H-Oxazolo(3,4-c)oxazole-7a(7H)-methanol
65447-77-0	Butanedioic acid, dimethyl ester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidineethanol (For colorant use only)
65530-66-7	Poly(difluoromethylene), α-fluoro-ω-[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]-
65530-85-0	alpha-(Cyclohexylmethyl)-omega-hydropoly(difluoromethylene)
65545-80-4	Poly(oxy-1,2-ethanediyl), alpha-hydro-omega-hydroxy-, ether with alpha-fluoro-omega-(2-hydroxyethyl)poly(difluoromethylene) (1:1)

CAS Reg. No.	Chemical Name
68585-36-4	Alkyl(C10-14)oxypoly(ethyleneoxy)ethyl phosphate
68585-47-7	Sulfuric acid, mono-C10-16-alkyl esters, sodium salts
68586-19-6	2-Propenoic acid, 2-methyl-, 2-((2,3,3a,4,7,7a(or 3a,4,5,6,7,7a)-hexahydro-4,7-methano-1H-indenyl)oxy)ethyl ester
68602-80-2	Distillates (petroleum), C12-30 aromatic
68603-15-6	Alcohols, C6-12
68603-16-7	Alcohols, C12-18, distn. residues
68603-17-8	Alcohols, C16-18, distn. residues
68603-18-9	C10-16 Alcohols distn. Residues
68603-23-6	Poly(oxy-1,2-ethanediyl),.alpha.-(carboxymethyl)-.omega.-hydroxy-, C11-15-sec-alkyl ethers, sodium salts
68603-42-9	Amides, coco, N,N-bis(2-hydroxyethyl)
68604-71-7	Imidazolium compounds, 1-{2-(2-carboxyethoxy)ethyl}-1(or 3)-(2-carboxyethyl)-4,5-dihydro-2-norc
68605-55-0	Fatty acids, tall-oil,polymers with bisphenol A,epichlorohydrin and tall oil
68605-57-2	Fatty acids, tall-oil, polymers with bisphenol A, epichlorohydrin, rosin and tung oil. (CA INDE
68606-06-4	Fatty acids, vegetable-oil, potassium sodium salts
68606-94-0	Oils, orange, sweet, terpene-free
68607-27-2	Dihydrogenated tallow hydroxyethyl methyl ammonium chloride
68607-29-4	Quaternary ammonium compounds, pentamethyltallow alkyltrimethylenedi-, dichlorides
68608-26-4	Sodium petroleum sulfonate
68608-66-2	Acetic acid, chloro-, sodium salt, reaction products with 4,5-dihydro-2-undecyl-1H-imidazole-1-ethanol and sodium hydroxide
68609-68-7	1-Hexanol, 2-ethyl-, manuf. of by-products from, distn. residues
68609-86-9	Manganese naphthanate 2-ethylhexanoate complex
68609-93-8	9-Octadecenoic acid (Z)-, sulfonated, Potassium salts
68610-19-5	Poly(oxy-1,2-ethanediyl), α,α'-[[methyl[3-(tridecyloxy)propyl]imino]di-2,1-ethanediyl
68610-44-6	Reaction products of methyl acrylate with 2-ethylhexylamine and sodium hydroxide
68610-92-4	Cellulose, omega-ether with alpha-?2-hydroxy-3-(trimethylammonio) propyl|-omega-hydroxypoly(oxy-1,2-ethanediyl) chloride
68611-14-3	Lignosulfonic acid, ethoxylated, sodium salts
68611-44-9	Silane, dichlorodimethyl-, reaction products with silica
68611-55-2	Sulfated mixed oxo alcohols (100% C10 and up)
68628-60-4	Benzenesulfonic acid, 4-sec-dodecyl-, sodium salt
68630-83-1	2-Propenoic acid, 2-methyl-, polymer with ethenylbenzene and alpha-hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)-(Z)-2-butenedioate
68630-92-2	Disodium 3-(2-(2-carboxyethoxy)ethyl)-2-heptyl-2,3-dihydro-1H-imidazole-1-propanoate
68630-96-6	1H-Imidazolium, 1-(2-carboxyethyl)-4,5-dihydro-3-(2-hydroxyethyl)-2-isoheptadecyl-, hydroxide, inner salt
68647-71-2	Tall oil, potassium salt

CAS Reg. No.	Chemical Name
68647-72-3	Terpenes, orange oil
68647-73-4	Oils, tea-tree
68647-95-0	Fatty acids, C18-unsatd., dimers, compds. with coco alkylamines
68648-12-4	Fatty acids, tall-oil, diesters with polypropylene glycol
68648-20-4	Fatty acids, tall-oil, sesquiesters with sorbitol, ethoxylated
68648-20-4	Sorbitol tall oil fatty acid sesquiester, ethoxylated
68648-35-1	Sulfonated cod oil
68648-38-4	Polyoxyethylene lanolin alcohol
68648-44-2	Pyrethrum marc
68648-50-0	Resin acids and Rosin acids, dimers, calcium salts
68648-72-6	Sodium alpha-olefin (C12-C16) sulfonate
68648-89-5	Benzene, ethenyl-, polymer with 2-methyl-1,3-butadiene, hydrogenated (CA INDEX NSME)
68648-98-6	Benzenesulfonic acid, mono-C7-17-branched alkyl derivs.
68649-00-3	Benzenesulfonic acid, mono-C9-17-branched alkyl derivs., compds. with 2-propanamine
68649-29-6	Polyethylene-polypropylene glycol, mono-C10-16-alkyl ethers, phosphates
68649-55-8	Poly(oxy-1,2-ethanediyl), [alpha]-sulfo-[omega]-(nonylphenoxy)-, branched, ammonium salt
68649-89-8	Resin acids and rosin acids, ammonium salts
68650-09-9	Polyoxyethylene* glycerol tall oil ester *(25 moles) (Mol. wt. 1490)
68650-28-2	Fatty acids, tall-oil, polymers with pentaerythritol, polyethylene glycol and trimellitic anhydride
68650-39-5	Imidazolium compounds, 1-(2-(carboxymethoxy)ethyl)-1-(carboxymethyl)-4,5-dihydro-2-norcoco alkyl, hydroxides, inner salts, disodium salts
68650-50-0	Fatty acids, C18-unsatd., dimers, polymers with ethylenediamine
687-47-8	Propanoic acid, 2-hydroxy-, ethyl ester (S)
68783-43-7	Fatty acids, linseed-oil, calcium salts
68783-78-8	Ditallow dimethyl ammonium chloride
68784-79-2	Sulfuric acid, mono-C15-18-alkyl esters, sodium salts
68813-94-5	Sulfuric acid, zinc salt, basic
68813-94-5	Zinc sulfate, basic
68814-56-2	Rhizobium japonicum
68814-57-3	Rhizobium leguminosarum
68814-58-4	Rhizobium lupini
68814-59-5	Rhizobium meliloti
68814-60-8	Rhizobium phaseoli
68814-61-9	Rhizobium trifolii
68815-61-2	Sulfuric acid, mono-C12-15-alkyl esters, ammonium salts
688-37-9	9-Octadecenoic acid, (Z)-, aluminum salt
68855-41-4	Lignosulfonic acid, sodium salt, oxidized
68855-54-9	Kieselguhr, soda ash flux-calcined
68855-99-2	Litsea cubeba oil
68876-77-7	Yeast
68890-70-0	Sulfuric acid, mono-C12-15-alkyl esters, sodium salts

CAS Reg. No.	Chemical Name
68890-80-2	Benzene, ethenyl-, polymer with 2,5-furandione, 2-butoxyethyl ester, ammonium salt
68891-11-2	Oxirane, methyl-, polymer with oxirane, mono(nonylphenyl) ether, branched
68891-13-4	Oxirane, methyl-, polymer with oxirane, mono-C10-16-alkyl ethers, phosphates, potassium salts
68891-21-4	Poly(oxy-1,2-ethanediyl),α-(dinonylphenyl)-ω-hydroxy-branched
68891-29-2	alpha-Alkyl(C8-C10)-omega-hydroxypoly(oxyethylene) ammonium sulfate
68891-33-8	Nonylphenol polyoxyethylene sulfate
68891-38-3	Alcohols, (C12-14), ethoxylated, monoethers with sulfuric acid, sodium salts
68908-46-3	Sulfuric acid, mono-C10-16-alkyl esters, potassium salts
68908-63-4	Ethoxylated C12-15 alcohols
68908-64-5	Poly(oxy-1,2-ethanediyl), α-hydro-. omega.-hydroxy-, mono-C10-12-alkyl ethers, phosphates
68909-20-6	Silanamine, 1,1,1-trimethyl-N-(trimethylsilyl)-, hydrolysis products with silica
68909-59-1	Phosphoric acid, mono-C8-10-alkyl esters, monosodium salts
68909-82-0	Naphthalenesulfonic acid, bis(1-methylethyl)-, Me derivs, sodium salts
68909-83-1	Naphthalenesulfonic acid, butyl-, Me derivs, sodium salts
68909-84-2	Naphthalenesulfonic acid, dibutyl-, Me derivs, sodium salts
68911-49-9	Dried blood
68911-87-5	Bis(hydrogenated tallow alkyl) dimethyl ammonium salts with montmorillonite
68915-31-1	Sodium hexametaphosphate ((NaPO3)6)
68915-32-2	Quassia extract
68916-18-7	Coffee grounds
68916-91-6	Licorice extract
68917-18-0	Cornmint oil
68917-19-1	Magnolia flower
68917-32-8	Terpenes and terpenoids, grapefruit-oil
68917-60-2	Terpenes and terpenoids, pennyroyal-oil
68917-71-5	Terpenes and terpenoids, lime-oil
68917-73-7	Oils, wheat
68917-75-9	Wintergreen oil
68918-78-5	Quaternary ammonium compounds, bis(C8-18 and C18-unsatd. alkyl)dimethyl, chlorides
68919-53-9	Fatty acids, soya, Me esters
68919-54-0	Sunflower-oil fatty acids, Me ester
68919-76-6	Fatty acids, tall-oil, reaction products with 2-{(2-aminoethyl)amino}ethanol
68920-66-1	Alcohols, C16-18 and C18-unsatd., ethoxylated
68920-69-4	Alcohols, C9-11, propoxylated
68921-42-6	Benzenemethanaminium, N-ethyl-N-(4-((4-(ethyl((3-sulfophenyl)methyl)amino)phenyl)(2-sulfophenyl)methylene)-2,5-cyclohexadien-1-ylidene)-3-sulfo-, hydroxide, inner salt, aluminum salt (3:2)
68928-85-8	Vinyl acetate, crotonic acid, vinyl neodecanoate, glycidyl methacrylate polymer
68937-10-0	Hydrogenated polyisobutene
68937-41-7	Phenol, isopropylated, phosphate (3:1)

CAS Reg. No.	Chemical Name
68937-54-2	Siloxanes and silicones, di-Me, 3-hydroxypropyl Me, ethoxylated
68937-55-3	Siloxanes and silicones, di-Me, 3-hydroxypropyl Me, ethoxylated propoxylated
68937-56-4	Siloxanes and silicones, di-Me,[(methylsilylidyne)tris(oxy)tris-, hydroxy terminated, ethers with polyethylene-polypropylene glycol monobutyl ether
68937-83-7	Fatty acids, C6-10, methyl esters
68937-84-8	Fatty acids, C12-18, methyl esters
68937-99-5	Sunflower seeds
68938-15-8	Fatty acids, coco, hydrogenated
68938-54-5	Siloxanes and silicones, di-Me, 3-hydroxypropyl Me, ethers with polyethylene glycol mono-Me eth
68951-67-7	Alcohols, C14-15, ethoxylated
68952-63-6	Linseed oil, tung oil, di-tert-butylphenol, bisphenol A, formaldehyde polymer
68953-01-5	Fatty acids, tall-oil, esters with ethoxylated sorbitol
68953-36-6	Tall oil fatty acids, reaction products with tetraethylene pentamine
68953-91-3	Benzenesulfonic acid, mono-C7-17-alkyl derivs., calcium salts
68953-96-8	Benzenesulfonic acid, mono-C11-13-branched alkyl derivs., calcium salts
6895-43-8	Ethyl bixin
68954-84-7	Poly(oxy-1,2-ethanediyl), alpha-(nonylphenyl)-omega-hydroxy-, branched, phosphates, sodium salts
68955-55-5	Amines, C12-14-alkyldimethyl, N-oxides
68955-64-6	Hexanedinitrile, hydrogenated, high-boiling fraction, phosphonomethylated
68956-56-9	Hydrocarbons, terpene processing by-products
68957-00-6	Siloxanes and Silicones, di-Me, Me hydrogen, reaction products with polypropylene glycol monoallyl ether
68959-25-1	3-Pentanol, 1-(2-hydroxyethoxy)-2,2,4-trimethyl-
68964-56-7	Octadecanoic acid, 9(or 10)-(sulfooxy)-, monosodium salt
689-82-7	2-Butenedioic acid (Z)-, monopotassium salt
68987-29-1	1-Octadecanol, phosphate, potassium salt
68987-63-3	Copper, [29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]-, chlorinated
68987-81-5	Ethoxylated propoxylated C6-10 alcohols-
68988-26-1	2-Butenedioic acid (2E)-,mixed esters with polyethylene glycol and polyethylene glycol mono(nonylphenyl) ether, polymer with methacrylic acid and styrene
68988-56-7	Polytrimethylhydrosilylsilicone
68988-76-1	9-Octadecenoic acid (Z)-, sulfonated
68989-01-5	Quaternary ammonium compounds, benzyl-C12-18-alkyldimethyl, salts with 1,2-benzisothiazol-3(2H)
68989-22-0	Zeolites, NaA
68990-15-8	Oils, fenugreek
68990-20-5	Penta cosolvent
68990-53-4	Glycerides, C14-22 mono-
68990-54-5	Glycerides, C14-22 mono-,acetates
68991-42-4	Oils, red pepper, paprika
68991-48-0	Alcohols, C7-21, ethoxylated
69009-90-1	1,1'-Biphenyl, bis(1-methylethyl)-

CAS Reg. No.	Chemical Name
69011-04-7	n-Butyl acid phosphate, manganese salt
69011-15-0	Benzene, diethenyl-, polymer with ethenylbenzene and ethenylethylbenzene, chloromethylated, 2-(dimethylamino)ethanol-quaternized
69011-22-9	Benzene, diethenyl-, polymer with etenylbenzene and ethenylethylbenzene, sulfonated, sodium salts
69011-36-5	Polyoxyethylene tridecyl (branched) alcohol
69011-37-6	Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-hydroxy-, C8-14-alkyl ethers, ammonium salts
69011-84-3	Poly(oxy-1,2-ethanediyl),α-sulfo-ω-(octylphenoxy)-,branched,sodium salt (CA INDEX NA
69012-32-4	Calcium silicate slag
69013-18-9	α-Alkyl(C8-C14)-omega-hydroxypoly(oxypropylene) block copolymer withpolyoxethylene; polyoxpropylene content averages 2 moles; polyoxyethylene content averages 7 moles
69029-39-6	Polyoxyethylene polyoxypropylene mono(di-sec-butylphenyl) ether
6915-15-7	Malic acid
69227-22-1	alpha-Alkyl*-omega-hydroxy-polyoxyethylene** polyoxypropylene*** polyoxyethylene** *(100% C10-C16) **(4 moles) ***(1.5 moles)
69278-92-8	Tall oil, calcium zinc salt
692-86-4	10-Undecenoic acid, ethyl ester
693-33-4	1-Hexadecanaminium, N-(carboxymethyl)-N.N-dimethyl-, inner salt
69364-63-2	Poly(oxy-1,2-ethanediyl), alpha-isohexadecyl-omega-hydroxy-
6938-94-9	Diisopropyl adipate
69430-24-6	Cyclosiloxanes, di-Me
69430-36-0	Hydrolyzed keratins
695-06-7	4-Hexanolide
69-65-8	Mannitol
69669-25-6	Fatty acids, C12-20, potassium salts
69669-36-9	Siloxanes and silicones, di-Me, 3-hydroxypropyl Me, Me 2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl, ethers with polyethylene-polypropylene glycol mono-Me ether
69671-09-6	Propylene-ethylene thioether
6969-49-9	Octyl salicylate
69-72-7	Salicylic acid
69-79-4	D-Glucose, 4-O-alpha-D-glucopyranosyl-
69808-32-8	3-Pyridinecarbonitrile, 1-butyl-5-[(4-chlorophenyl)azo]-1,2-dihydro-6-hydroxy-4-methyl-2-oxo-
69867-71-6	Phosphoric acid, monopentyl monophenyl ester
69898-00-6	alpha-Olefins
69-93-2	Uric acid
6994-46-3	C.I. Solvent Blue 59
70084-87-6	Glutens, enzyme-modified
7011-83-8	Decanoic acid, 4-hydroxy-4-methyl-,.gamma.-lactone
70131-50-9	Acid-leached bentonite
70131-67-8	Dimethyl siloxane, hydroxy-terminated

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CAS Reg. No.	Chemical Name
	naphthalenolato(2-)}-, sodium
73513-47-0	Disodium zinc ethylenediaminetetraacetate
73637-19-1	Disodium cupric ethylenediaminegtetraacetate trihydrate
73637-20-4	Disodium manganese ethylenediaminetetraacetate
73728-37-7	Rubber, cyclized
7373-11-7	2-Hydroxypropylamine nitrite
73772-32-4	1-Propanesulfonic acid, 3-{{-(dimethylamino)propyl}{(tridecafluorohexyl)sulfonyl}amino}-2-hydro
7378-99-6	1-Octanamine, N,N-dimethyl-
7379-27-3	Potassium ethylenediaminetetraacetate
7379-28-4	Glycine, N,N'-1,2-ethanediylbis(N-(carboxymethyl)-, sodium salt
73807-20-2	Fatty acids, tall-oil, polymers with bisphenol A, diethylenetriamine, epichlorohydrin and triethylenetetramine
73891-88-0	Tannic acid
73891-99-3	Rape oil, Me ester
74204-30-1	Benzoic acid, 2-{{2-hydroxy-5-sulfo-3-{(2,5,6-trichloro-4-pyrimidinyl) amino}phenyl}imino}-1-phenylethyl}azo}-5-sulfo-, copper complex
7429-90-5	Aluminum (metal)
7439-89-6	Iron (Fe)
7440-37-1	Argon
7440-44-0	Carbon
7440-50-8	Copper
7440-59-7	Helium
7440-66-6	Zinc (metallic)
7443-25-6	Propanedioic acid, {(4-methoxyphenyl)methylene}-, dimethyl ester
7446-19-7	Zinc sulfate monohydrate
7446-20-0	Sulfuric acid, zinc salt (1:1), heptahydrate
7446-26-6	Zinc pyrophosphate
7446-70-0	Aluminum chloride
7447-40-7	Potassium chloride (KCl)
7447-41-8	Lithium chloride
74499-22-2	Methyl tallate
74504-64-6	1,2,3-Propanetriol, homopolymer, dodecanoate
74775-06-7	Poly{oxy(methyl-1,2-ethanediyl)},α-(1-oxopropyl)-ω-(tetradecyloxy)-
74811-65-7	Croscarmellose sodium
74-84-0	Ethane
74-86-2	Acetylene
7487-79-8	Diethanolamine laurate
7487-88-9	Magnesium sulfate
7492-30-0	9-Octadecenoic acid, 12-hydroxy-, monopotassium salt, (9Z, 12R)-
74-98-6	Propane
75-01-4	Ethene, chloro-
75-05-8	Acetonitrile
75-28-5	Isobutane

CAS Reg. No.	Chemical Name
8022-37-5	Armoise Oil
8022-56-8	Oils, sage
8023-74-3	Mink oil
8023-77-6	Resins, oleo-, capsicum
8024-32-6	Fats and glyceridic oils, avocado
80-26-2	3-Cyclohexene-1-methanol, α,α,4-trimethyl-, acetate
80-27-3	α-Terpinyl propionate
8027-33-6	Alcohols, lanolin
8028-48-6	Sweet orange peel tincture
8028-52-2	Vinegar (maximum 8% acetic acid in solution)
8028-66-8	Honey
8028-89-5	Caramel
8029-31-0	Beer
8029-76-3	Hydroxylated lecithin
8030-12-4	Tallow hydrogenated
8030-30-6	Petroleum Naphtha
8030-76-0	Lecithins, soya
8030-78-2	Tallow trimethyl ammonium chloride
8031-18-3	Fuller's earth
8039-09-6	Ethoxylated lanolin
80-39-7	N-Ethyl-p-tolylsulfonamide
8042-47-5	Mineral Oil U.S.P.
8042-47-5	White mineral oil (petroleum)
80-46-6	p-tert-Amylphenol
8046-71-7	Soaps
8046-74-0	Soaps, potassium
8047-99-2	Ethyl toluene sulfonamide
8049-98-7	Milk
8049-99-8	Milorganite
8050-07-5	Olibanum
8050-09-7	Rosin (wood)
8050-13-3	Methyl hydrogenated rosinate
8050-15-5	Methyl ester of rosin, partially hydrogenated
8050-26-8	Resin acids and Rosin acids, esters with pentaerythritol
8050-31-5	Resin acids and rosin acids, esters with glycerol
8050-33-7	Polyoxyethylene* ester of rosin *(10-15 moles)
8050-81-5	Simethicone
8052-10-6	Tall oil rosin
8052-35-5	Molasses
8052-41-3	Stoddard solvent
8052-42-4	Asphalt
8052-48-0	Fatty acids, tallow, sodium salts
8052-50-4	Tallow, sulfated, sodium salt
80-54-6	Benzenepropanal, 4-(1,1-dimethylethyl)-α-methyl-
80-56-8	alpha-Pinene

CAS Reg. No.	Chemical Name
84501-72-4	Sodium isononanoate
84540-57-8	Propylene glycol monomethyl ether acetate
84604-14-8	Extract of rosemary
84-66-2	Diethyl phthalate
846-70-8	2-Naphthalenesulfonic acid, 8-hydroxy-5,7-dinitro-, disodium salt
84681-71-0	Hydrogenated rapeseed oil
84696-51-5	Spearmint, ext.
84-74-2	Dibutyl phthalate
84775-78-0	Kelp
84-88-8	5-Quinolinesulfonic acid, 8-hydroxy-
84929-31-7	Lemon extract
84961-66-0	Tobacco dust
85049-30-5	Bentonite, sodian
85116-93-4	Fatty acids, C16-18, esters with pentaerythritol
85261-20-7	D-Glucitol, 1-deoxy-1(methylamino)-, N-C10 acyl derivs.
85-40-5	4-Cyclohexene-1,2-dicarboximide
85-41-6	Phthalimide
85-44-9	Phthalic anhydride
85536-14-7	Benzenesulfonic acid, 4-C10-13-sec-alkyl derivs.
85585-93-9	Carbonic acid, aluminum magnesium salt, basic
85637-75-8	Oxirane, methyl-, polymer with oxirane, mono[2-(2-butoxyethoxy)ethyl] ether
85665-95-8	7-Benzothiazolesulfonic acid, 2-{4-{{4-{{3-{{5-(aminocarbonyl)-1- ethyl-1,6-dihydro-2-hydroxy-4-m
85-68-7	Butyl benzyl phthalate
85711-55-3	Fatty acids, tall-oil, compds. with oleylamines
85763-69-5	Iron, C3-13-carboxylate naphthenate complexes
85828-89-3	Chromium, 2-[(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1H-pyrazol-4-yl)azo]benzoate 2-[4,5-dihydro-3
85-83-6	C.I. Solvent Red 24
85-86-9	2-Naphthalenol, 1-((4-(phenylazo)phenyl)azo)-
860-22-0	FD&C Blue No. 2
86352-09-2	Naphthalenesulfonic acids, polymers with formaldehyde, sodium salts
86356-61-8	1-(2',5'-Dichloro-4'-sulfophenyl)-3-methyl-4-((4"-(N-polyoxyalkylene sulfonamide)phenyl)azo)pyrazol-5-one, sodium salt
864277-75-8	Lignoflex
866-83-1	Potassium citrate, monobasic
866-84-2	Potassium citrate
868-18-8	Sodium tartrate
86864-96-2	2-Propenoic acid, polymer with 2-hydroxypropyl 2-propenoate and sodium 2-propenoate
868662-38-8	Poly(oxy-1,2-ethanediyl), alpha-methyl-omega-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl) oxy] disiloxanyl]) propoxy]
86893-19-8	Ethoxylated methyl glucoside dioleate
87-01-4	7-(Dimethylamino)-4-methylcoumarin
87157-58-2	D-Glucitol, 1-deoxy-1(methylamino)-, N-C14 acyl derivs.

CAS Reg. No.	Chemical Name
9069-94-7	Dimethyl 5-sodiosulfoisophthalate-dimethyl terephthalate-ethylene glycol-polyethylene glycol copolymer
9071-85-6	Poly(oxy-1,2-ethanediyl), α,α'-phosphinicobis(ω-(nonylphenoxy)-
90-72-2	Phenol, 2,4,6-tris{(dimethylamino)methyl}-
9079-33-8	Poly(oxy-1,2-ethanediyl), .alpha.,.alpha.',.alpha.'',.alpha.'''-[[(2-sulfophenyl)methyliumylidene]bis(4,1-phenylenenitrilodi-2,1-ethanediyl)]tetrakis[.omega.-hydroxy-, chloride, monosodium salt
9079-34-9	Poly(oxy-1,2-ethanediyl), .alpha.,.alpha.',.alpha.'',.alpha.'''-[[(2-sulfophenyl)methyliumylidene]bis[(3-methyl-4,1-phenylene)nitrilodi-2,1-ethanediyl]]tetrakis[.omega.-hydroxy-, chloride, monosodium salt
90-80-2	Glucono-delta-lactone
9081-17-8	Nonylphenol, ethoxylated, monoether with sulfuric acid
9082-00-2	Oxirane, methyl-, polymer with oxirane, ether with 1,2,3-propanetriol (3:1)
9084-06-4	Naphthalenesulfonic acid, polymer with formaldehyde, sodium salt
9086-75-3	Poly(oxy-1,2-ethanediyl), alpha-(phenylmethyl)-omega-((1,1,3,3-tetramethylbutyl)phenoxy)-
9087-53-0	Polyethylene-polypropylend glycol hexadecyl ether
91031-95-7	Mannitan coconut oil ester
91051-70-6	Propylene glycol tall oil ester
91078-64-7	Naphthalenesulfonic acids, branched and linear Bu derivs., sodium salts
91-20-3	Naphthalene
91-53-2	Ethoxyquin
915-67-3	2,7-Naphthalenedisulfonic acid, 3-hyroxy-4-((4-sulfo-1-naphthyl)azo)-, trisodium salt
91697-98-2	Glycerides, C8-18 and C18-unsatd. mono-
91994-94-4	Acetylated lanolin alcohol
92129-90-3	Whey
92257-31-3	2-Naphthalenol ((phenylazo) phenyl) azo alkyl derivatives.
928-72-3	Glycine, N-(carboxymethyl)-, disodium salt
928-96-1	3-Hexen-1-ol, (3Z)-
93-08-3	2'-Acetonaphthone
93385-02-5	1-Propanol, 2-(tetradecyloxy)-,acetate
93385-03-6	3,6,9,12-Tetraoxaoctacosan-1-ol, 11-methyl, acetate
93-56-1	Phenyl glycol
93763-70-3	Perlite, expanded
93-83-4	9-Octadecenamide, N,N-bis(2-hydroxyethyl)-, (Z)-
93858-51-6	Benzenesulfonic acid, dodecyl-, compd. with 3-methoxy-1-propanamine (1:1)
93-89-0	Benzoic acid, ethyl ester
93918-16-2	Manganese neononoate
93-92-5	Benzenemethanol,α-methyl-,acetate
94-09-7	Ethyl p-aminobenzoate
94-13-3	Propyl p-hydroxybenzoate
94133-90-1	1-Propanesulfonic acid, 3-{{3-(dimethylamino)propyl}{(heptadecafluorooctyl)sulfonyl}amino}-2-hy
94133-91-2	1-Propanaminium, 3-{{(heptadecafluorooctyl)sulfonyl}(2-hydroxy-3-

CAS Reg. No.	Chemical Name
N/A	Cotton
N/A	Diethanolamide of methyl laurate
N/A	Dog or cat collar
N/A	Douglas fir bark
N/A	Egg Shells
N/A	Fatty acids, sunflower-oil, conjugated, polymers with maleic anhydride, and tall-oil fatty acids
N/A	Feldspathoid (alkali aluminosilicate mimeral)
N/A	Flavoring
N/A	Fumaric acid-isophthalic acid-styrene-ethylene/propylene glycol copolymer (minimum average mole
N/A	Granite
N/A	Imidazolium compds, 2-heptadecyl-4,5-dihydro-1-methyl-1-(2-tallow amidoethyl), Me sulfates
N/A	Iron humate
N/A	Malt flavor
N/A	Meat meal
N/A	Meat scraps
N/A	Medicated feed
N/A	Millet seed
N/A	Mineral wool (tile)
N/A	Mixed Phytosterols (consisting of campesterol, sitosterol)
N/A	N-(Soya alkyl)-N-methylmorpholinium sulfate
N/A	N,N'-1,3-xylyl bis(12-hydroxystearamide)
N/A	N,N-Dimethyl oleyl-linoleylamine salt of benzoic acid
N/A	Naphthalenesulfonic acid, isopropylisohexyl-, sodium salt
N/A	Nutria meat
N/A	Nylon
N/A	Oyster shells
N/A	Paper
N/A	Paprika
N/A	Paraffin wax
N/A	Peanut butter
N/A	Peanut shells
N/A	Peat moss
N/A	Propylene glycol isobutyl ether and higher homologs
N/A	Pumice
N/A	Red cabbage color, expressed from edible red cabbage heads via a pressing process using only acidified water
N/A	Red cedar chips
N/A	Rubber
N/A	Sawdust
N/A	Seaweed, edible
N/A	Soy protein
N/A	Soybean hulls

Attachment. 8. section 3

U.S. Food and Drug Administration
Department of Health and Human Services
CENTER FOR FOOD SAFETY AND APPLIED NUTRITION

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CFSAN/Office of Food Additive Safety
July 2006

FOOD ADDITIVE STATUS LIST

Formerly called Appendix A of the Investigations Operations Manual (IOM); New items are highlighted in yellow. If you are using an older web browser and you do not see the highlighting, you may download this document in PDF (270 KB) for printing.

Forward | Abbreviations | Color Additive Status List

A B C D E F G H I J K L M N O P Q R S T U V W X Y Z

DEC 15 2008

FOREWORD

This Food Additives Status List organizes additives found in many parts of 21 CFR into one alphabetized list. Additives included are those specified in the regulations promulgated under the FD&C Act, under Sections 401 (Food Standards), and 409 (Food Additives). The list also includes selected pesticide chemicals from 40 CFR 180 for which EPA has set tolerances in food. FDA enforces those tolerances. Within the space available, the Food Additives Status List includes use limitations and permitted tolerances for each additive. For complete information on its use limitations, refer to the specific regulation for each substance. New regulations and revisions are published in current issues of the Federal Register as promulgated. Also refer to the CFSAN website on Food Additives and Premarket Approval to review several FDA databases of additive categories. For example, EAFUS (Everything Added to Food in the United States) is a helpful reference within the limitations described at the beginning of the database.

The Food Additive Status List omits certain categories of additives. Here are the omissions:

1. Obviously safe substances not cited in a regulation as Generally Recognized as Safe (GRAS). You may find such substances on an FDA web site, which contains GRAS notifications received from companies since 1998, and FDA's response.
2. Synthetic flavoring substances in 21CFR 172.515. The CFR does not contain a complete list of permissible flavorings. Certain trade groups such as the Flavor Extract Manufacturers Association have established expert panels to evaluate and make determinations on the GRAS status of their products. If you need help in determining the acceptability of a flavoring after consulting 21 CFR 172.515, contact CFSAN Office of Food Additive Safety (HFS-200) at (301) 436-1200.
3. Those pending administrative determination.
4. Substances granted prior sanction for specific use prior to enactment of the Food Additives Amendment. For additional information on these substances, contact the CFSAN Office of Food Additive Safety (HFS-200) at (301) 436-1200.
5. Indirect food additives, 21 CFR Parts 175, 176, 177, & Part 178 (except that sanitizing agents for food processing equipment as listed in 178.1010 are included in the Food Additives list.) Be aware that as a result of the Food Quality Protection Act of 1996 and Antimicrobial Regulation Technical Corrections Act of 1998, EPA now has jurisdiction

over sanitizing solutions applied to permanent or semi-permanent food contact surfaces, other than food packaging. To look up indirect food additives in Parts 175, 176, 177 and 178 go to FDA's "List of Indirect Additives Used in Food Contact Substances". Use it to locate the regulation in which its use is fully described. FDA has recently implemented a new way to market, called "Premarket Notification", for certain food contact substances. These notifications are effective only for the manufacturer or supplier identified in the notification. A list of effective notifications is available on the FDA website.

6. Color additives, 21 CFR Parts 70, 71, 73, 74, 80 & 82. Go to the Color Additives Status List following the Food Additives Status list in Appendix A.

NOTE: The Food Additives Status List is provided only as a quick look-up on the use limitations for a food additive or pesticide chemical. It is possible that mistakes or omissions could have occurred. Additionally, there may be cases where the agency has offered interpretations concerning specific provisions of the regulations. For example, in the case of boiler water additives or other minor ingredients, processing aids, or indirect additives, FDA has not objected, in certain cases, to the substitution of ammonium, calcium, magnesium, potassium, or sodium salts for each other when only one is listed in a regulation. The Food Additive Status list is updated annually, so it may not reflect the latest information. For all these reasons, take care before advising a firm that a use of a particular food additive is prohibited or otherwise limited. Read the actual regulation. If there are any doubts or if a particular situation is unclear, you or your supervisor should consult with the CFSAN, Office of Food Additive Safety (HFS-200) at (301) 436-1200, or the Division of Petition Review (HFS-265) at (301) 436-1264, or the Division of Food Contact Substance Notification Review HFS-275 at (301) 436-1162, or the Division of Biotechnology and GRAS Notice Review HFS-255 at (301) 436-1221.

Please send corrections or additions to the list to Harold Woodall, FDA/CFSAN Office of Food Additive Safety (HFS-206), 5100 Paint Branch Parkway, College Park, Maryland 20740 or e-mail them to harold.woodall@fda.hhs.gov.

ABBREVIATIONS USED

Technical Effects

Type	Kind, effect or use of additive	Type	Kind, effect or use of additive
AC	Anticaking agent	AF	Antifoaming (or defoaming) agent
AOX	Antioxidant	BC	Boiler compound
BL	Bleaching agent or flour-maturing agent	B&N	Buffer and neutralizing agent
CTG	Component or coating for fruits & vegetables	DS	Dietary supplement
EMUL	Emulsifier	ENZ	Enzyme
ESO	Essential oil and/or oleoresin (solvent free)	FEED	Substances under the Food Additives Amendment added directly to feed
FLAV	Natural flavoring agent	FL/ADJ	Substance used in conjunction with flavors
FUM	Fumigant	FUNG	Fungicide
HERB	Herbicide	HOR	Hormone
INH	Inhibitor	MISC	Miscellaneous

NAT	Natural substances and extractives	NNS	Non-nutritive sweetener
NUTR	Nutrient	NUTRS	Nutritive Sweetener
PEST	Pesticide other than fumigant	PRES	Chemical preservative
SANI	Sanitizing agent for food processing equipment	SDA	Solubilizing and dispersing agent
SEQ	Sequestrant	SOLV	Solvent
SP	Spices, other natural seasonings & flavorings	SP/ADJ	Spray adjuvant
STAB	Stabilizer	SY/FL	Synthetic flavor
VET	Veterinary drug, which may leave residue in edible tissues of animals or in edible animal products		

Status

Type	Kind, effect or use of additive	Type	Kind, effect or use of additive
BAN	Substances banned prior to the Food Additives Amendment (FAA) because of toxicity. These substances are bolded and italicized.	FS	Substances permitted as optional ingredient in a standardized food
GRAS	Generally recognized as safe. Substances in this category are by definition, under Sec. 201(s) of the FD&C Act, not food additives. Most GRAS substances have no quantitative restrictions as to use, although their use must conform to good manufacturing practices. Some GRAS substances, such as sodium benzoate, do have a quantitative limit for use in foods.	GRAS/FS	Substances generally recognized as safe in foods but limited in standardized foods where the standard provides for its use.
ILL	Substances used or proposed for use as direct additives in foods without required clearance under the FAA. Their use is illegal. These substances are bolded and italicized.	PD	Substances for which a petition has been filed but denied because of lack of proof of safety. Substances in this category are illegal and may not be used in foods.
PS	Substances for which prior sanction has been granted by FDA for specific uses. There are a number of substances in this category not listed herein because they have not been published in the FEDERAL REGISTER.	REG	Food additives for which a petition has been filed and a regulation issued.
REG/FS	Food additives regulated under the FAA and included in a specific food standard.		

Other

Type	Kind, effect or use of additive	Type	Kind, effect or use of additive
&	and	amt	amount
art	artificially	avg	average
ca	about, approximately	calc	calculated
CFR	Code of Federal Regulations	cnd	canned
cond	conditions	comb.	w/ in combination with; combined with
comp	component	ctg	coating for fruits, vegetables, tablets
do	Same CFR reference as appears earlier in	dr	dried

	paragraph		
F.R.	Federal Register	g	gram(s)
GMP	In accordance with good manufacturing practices; or sufficient for purpose; or quantity not greater than required	incl	including
mfr	manufacture	mg	milligram(s)
min	mineral	ml	milliliter
nonstdzd	nonstandardized	Part	Refers to Part number under Title 21 CFR
pdt	product	pdtn	production
pest	pesticide	pkg	packaging
ppm	parts per million	prepns	preparations
res	residue	sp	special dietary
suppl	supplement	sw	sweetened
tabs	tablets	temp	temporary
veg	vegetable(s)	w/	with
w/o	without	wt	weight
X-ref	cross reference	<	less than
≤	less than or equal to	>	greater than
≥	greater than or equal to	+	plus

A

Acacia (gum arabic)- EMUL/STAB, REG, Used as thickener, emulsifier, or stabilizer at ≤20% of alcoholic beverages-172.780, GRAS/FS, See Reg Part 135, Frozen Desserts; Part 169, Food Dressings and Flavorings; Part 169.179, Vanilla Pwd-184.1330

Acephate - PEST, REG, 40 CFR 180.108

Acesulfame potassium - NNS, REG, See Regulation -172.800

Acetic acid - B&N/FEED, GRAS/FS, Part 133, Cheese; Part 582.1005, In animal feed practices; 184.1005, 172.814

Acetic anhydride - MISC, REG, In modifying food starch -172.892

Acetone - SOLV, REG, 30 ppm - As residual solvent in spice oleoresins 173.210

Acetone peroxides - BL, REG/FS, GMP, Part 137, Cereal Flours -172.802

Acetyl-(p-nitrophenyl)-sulfanilamide - FEED, REG, See: Sulfanitran

N-Acetyl-L-Methionine (free, hydrated, or anhydrous, or sodium or potassium salts) - NUTR, REG, In foods, except infant foods and foods containing added nitrites/nitrates - 172.372

Acetylated monoglycerides - EMUL, REG, GMP, Used in food, food processing, food pkg or food stg equipment -172.828

Acidified sodium chlorite solutions - REG, Microbial control agent in water for processing poultry, raw agricultural commodities, processed fruits, processed root, tuber, bulb, legume, fruiting (i.e., eggplant, groundcherry, pepino, pepper, tomatillo, and tomato), curcurbit and leafy vegetables, red meat, red meat parts, organs, processed, comminuted exceed 0.3 gram cetylpyridinium chloride per pound of raw poultry carcass. The solution shall also contain propylene glycol at a concentration of 1.5 times that of the cetylpyridinium chloride-173.375

Chamomile Flower - SP, REG - 182.10

Chamomile Flower, English, Oil - ESO, REG - 182.20

Chemicals for controlling micro-organisms in cane sugar and beet sugar mills-REG 173.320

Chemicals used in delinting cottonseed - 173.322

Chemicals used in washing fruits & vegs. or to assist in peeling fruits and vegs. Polyacrylamide, Potassium bromide, Sodium dodecylbenzenesulfonate, Sodium hypochlorite, sodium 2-ethyl-l- hexylsulfate, sodium n-alkylbenzene sulfonate, sodium mono- and dimethyl-naphthalene sulfonates- mol wt 245-260, Alkylene oxide adducts of alkyl alcohols and phosphate esters of alkylene oxides. Adducts of alkyl alcohols mixtures -MISC, REG, Use of chemicals followed by rinsing to remove residues. X-ref - Individual chemicals, 173.315 limits amounts of some in wash water

Cherry-laurel leaves - FL/ADJ, REG, GMP, In conjunction w/flavors only; <25 ppm prussic acid - 172.510

Cherry-laurel water - FL/ADJ - 172.510

Cherry, pits, extract - FL/ADJ, REG, GMP, In conjunction w/flavors only; <25 ppm prussic acid - 172.510

Cherry, wild, bark - ESO, GRAS - 182.20

Chervil - ESO/SP/FLAV, GRAS - 182.10

Chervil extract -ESO, GRAS - 182.20

Chestnut leaves/extract - FL/ADJ, REG, In conjunction w/flavors - 172.510

Chewing gum base, MISC, REG, GMP, Chicle, chiquibul, crown gum, gutta hang kang, jelutong, massaranduba balata, massaranduba chocolate, nispero, lechi caspi, pendare, perillo, rosidinha, Venezuelan chicle, Leche de vaca, Niger gutta, tunu, chilte, natural rubber, glycerol ester of tall oil resin, etc. - 172.615

Chicle - MISC, REG, Comp of chewing gum base - 172.615

Chicory - ESO, GRAS - 182.20

Chilte - MISC, REG, Chewing gum base - 172.615

Chilquibul - MISC, REG, Comp of chewing gum base -172.615

Chirata (Chiretta, East Indian Bolonong) & herb extract

- FL/ADJ, REG, GMP, In alcoholic beverages only - 172.510 Chives - SP, GRAS - 182.10

Chloramphenicol - VET, REG, ZERO - Drug in any form may not be used in food (meat, milk, and egg) producing animals

Chlorhexidine dihydrochloride -VET, REG, ZERO Residue in edible tissues of calves - 556.120

Chlorimuron ethyl - PEST, REG, Tolerance for Residues 40 CFR 180.429

Chlorine & chlorine dioxide - BL, FS, GMP, Part 137, Cereal Flours

Chlorine dioxide - MISC, REG, Used as an antimicrobial agent in poultry process water at a

Cyhexatin - INSECT, REG, Use: In animal feed -Tolerances for Residues 40 CFR 180.144

Cyromazine - PEST, REG, Tolerances for Residues 40 CFR 180.414

Cysteine (l-form) - MISC, FS, 0.009 parts per 100 parts flour by wt. - Part 136 - Bakery Products; 184.1271; 184.1272; NUTR/DS, REG - 172.320

Cysteine (l-form) monohydrochloride - MISC, GRAS -184.1272 - Used to supply up to 0.009 part of total L-cys-teine per 100 parts of flour in dough as a dough strengthener

Cystine (l form) - NUTR/DS, REG - 172.320

D

Damar Gum (Shorea dipterocarpaceae) - Diluents in color additives - 73.1

2,4-D (2,4-dichlorophenoxyacetic acid) - PEST, REG, 2 ppm - Tolerances for Residues - 40 CFR 180.142

Damiana leaves - FL/ADJ, REG, GMP, In conjunction w/flavors - 172.510

Dandelion, dandelion root - ESO, GRAS,

Dandelion, fluid extract (Taraxacum spp.) - GRAS -182.20

DDVP - FEED, REG, See Dichlorvos

Decalactone alone or comb/w dodecalactone - FLAV, REG, <10 ppm alone or <20 ppm comb - As artificial flavoring in oleomargarine. Part 166 - 172.515

Decanoic Acid - SANI, REG, 109 - 218 ppm total fatty acids - Component of sanitizing solution - 178.1010, Coating for fruits and vegetables - 172.210, Fatty acids -172.860, Defoaming agents - 173.340

1-Decanol - SYN fatty alcohol - 172.864

Decoquinate - FEED, REG, 2 ppm - In uncooked edible tissue, other than skeletal muscle, of chicken and goats as a residue - 556.170; 1 ppm - In skeletal muscle of chickens as a residue - 556.170; Use: In dry and liquid medicated feed - 558.195

Decyl alcohol, synthetic - MISC, REG, GMP, See Fatty alcohols, synthetic - 172.864

Defoaming agents and components Dimethylpolysiloxane, polyoxyethylene 40 monostearate, Polysorbate 60, Polysorbate 65, propylene glycol alginate, silicon dioxide, sorbitan monostearate, aluminum stearate (For use in processing beet sugar and yeast only - 173.340); **butyl stearate, BHA, BHT, calcium stearate, fatty acids, hydroxylated lecithin, isopropyl alcohol, magnesium stearate, mineral oil, petrolatum, odorless light petroleum hydrocarbons, Petroleum waxes, Synthetic isoparaffinic petroleum hydrocarbons, Oxystearin, Polyethylene glycol, Polyoxyethylene (600) dioleate, Polyoxyethylene (600) mono-ricinoleate, polypropylene glycol, polysorbate 80, potassium stearate, propylene glycol mono & diesters of fats and fatty acids, soybean oil fatty acids - hydroxylated; tallow - hydrogenated, oxidized, or sulfated; hydrogenated tallow alcohol. n-Butoxypolyoxyethylene** (AF, REG, For use in processing beet sugar only - 173.340); **polyoxypropylene glycol formaldehyde, sodium polyacrylate, synthetic petroleum wax, oleic acid from tall oil fatty acids** - AF, REG, In foods. See individual chemicals for uses and limitations - 173.340

Defoaming agents, butter, oleomargarine, lard, corn oil, coconut oil, cottonseed oil, mono- and diglycerides of fat-forming fatty acids - AF, REG/FS, GMP, In fruit butters, jellies, preserves and related products - Part 150

Glutamine - NUTR, REG, (See specs in 172.320)

Glutaraldehyde - MISC, GMP, Fixing agent for the immobilization of gloucose isomerase for use in the manufacture of high fructose corn syrup, in accordance with Sec. 184.1372 - 173.357

Glycerides and polyglycides of hydrogenated vegetable oils - MISC, Used as an excipient in dietary supplement tablets, capsules, and liquid formulations - See 172.736 for specifications and limitations.

Glycerin - MISC, GRAS/FS, GMP, Part 169, Food Flavorings, 182.1320; Part 582 - Animal feeds

Glycerin, synthetic - MISC, REG, GMP, In food. (See 172.866 for specs)

Glycerol - See glycerin

Glycerol ester of gum rosin - MISC, REG, ≤100 ppm in beverages - 172.735; GMP, Softener for chewing gum base (See specs in 172.615)

Glycerol ester of partially dimerized rosin - MISC, REG, GMP, Comp of chewing gum base (See specs in 172.615)

Glycerol ester of partially hydrogenated gum or wood rosin - MISC, REG, GMP, Comp of chewing gum base (See specs in 172.615)

Glycerol ester of polymerized rosin - MISC, REG, GMP, Softener for chewing gum base (See specs in 172.615)

Glycerol ester of tall oil rosin - MISC, REG, GMP, Softener for chewing gum base (See specs in 172.615)

Glycerol ester of wood rosin - MISC, REG, ≤100ppm in beverages-172.735; GMP, Softener for chewing gum base-172.615

Glycerol (glyceryl) tributyrate (tributyrin, butyrin) -SY/FL, GRAS, GMP - as flavoring agent and adjuvant -184.1903

Glyceryl behenate - MISC, GRAS, GMP, As formulation aid in tablets - 184.1328

Glyceryl-lacto esters of fatty acids - EMUL, MISC, REG, GMP - 172.852

Glyceryl monooleate - MISC, GRAS, SY/FL, GMP, As flavoring agent and adjuvant - 184.1323

Glyceryl (glycerol) monostearate (monostearin) - MISC, GRAS/FS, GMP, 184.1324; <2% of product - Macaroni products - 139.110; <3% of product - Noodle products -139.150

Glyceryl palmitostearate - GRAS, GMP, Use as a formulation aid in excipients for tabs - 184.1329

Glyceryl triacetate (triacetin) - MISC, SY/FL, GRAS, GMP. As flavoging agent and adjuvant - 184.1901

Glyceryl tristearate - MISC, REG, See Reg - 172.811

Glycine - MISC, REG, 0.2% of fin bev or bev base Masking agent for saccharin in beverages & bases -172.812; STAB, 0.02% - In mono- and diglycerides -172.812; NUTR - 172.320

Glycoryrrhiza - SP/ESO, GRAS, See Reg - 184.1408

Glycyrrhizin, ammoniated - ESO, GRAS/FS, See Reg -184.1408

172.510

Rhubarb root - FL/ADJ, REG, GMP, In conjunction w/flavors - 172.510

Riboflavin - NUTR/DS, GRAS/FS, Cereal Flours - Part 137; Alimentary Pastes - Part 139; Bakery Prods - Part 136; GRAS, GMP - 182.5695, 184.1695

Riboflavin-5-phosphate - NUTR/DS, GRAS, GMP -182.5697, 184.1697

Rice bran wax - CTG/MISC, REG, < 50 m - Ctg for candy - 172.890;< 50 ppm - Ctg for fresh fruits & vegs -72.890; < 2.5% - In chewing gum as plasticizing material - 172.890, 172.615

Robenidine HCl - FEED, REG, 0.2 ppm - As residue in chicken fat & skin - 556.580; 0.1 ppm neg residue - In other edible tissue of chickens - 556.580; Use & other info - 558.515

Rose absolute (otto of roses, attar of roses) - ESO, GRAS - 182.20

Rose buds, flowers, fruit (hips), leaves - ESO, GRAS

Rose geranium - ESO, GRAS - 182.20

Roselle - FL/ADJ, REG, GMP, In alc bevs only - 172.510

Rosemary - SP/ESO, GRAS - 182.10, 182.20

Rosidinha (rosadinha) - MISC, REG - 172.615

Rosin (colophony) - FL/ADJ, REG, GMP, In alc bevs only -172.510

Rosin, gum, glycerol ester - MISC, REG, GMP, Softener for chewing gum - 172.615

Rosin, gum or wood, pentaerythritol ester, partially hydrogenated pentaerythritol ester, or partially hydrogenated glycerol ester - MISC, REG, GMP, Softener for chewing gum - 172.615

Rosin, methyl ester, partially hydrogenated - MISC, REG, GMP, Softener for chewing gum - 172.615; SY/FL -172.515

Rosi, partial dimerized, calcium salt or partially (catalytically) hydrogenated - CTG, REG, GMP, Ctg on fresh citrus fruit - 172.210

Rosin, polymerized glycerol ester, partially hydrogenated glycerol ester, or partially dimerized glycerol ester -MISC, REG, Softener for chewing gum - 172.615

Rosin, tall oil, glycerol ester-MISC, REG, GMP, Softener for chewing gum - 172.615

Rosin, wood - CTG, REG, GMP, Ctg on fresh citrus fruit -172.210

Rosin, wood, glycerol ester - MISC, REG, GMP, Softener for chewing gum - 172.615; MISC, REG - 172.735

Rosin, wood, pentaerythritol ester of maleic anhydride - CTG, REG, GMP, Ctg on fresh citrus fruit - 172.210

Roxarsone - FEED/VET, REG, See 3-nitro 4-hydroxy phenyl arsenic acid (Arsenic) for tolerances - 556.60; Use: In chicken & swine feeds - 558.530; In Drinking Water of chickens, turkeys, & swine - 520.2087, 520.2088

Rubber, butadiene-styrene - MISC, REG, Comp of chewing gum base - 172.615

Rubber (natural) smoked sheet and latex solids -MISC, REG, Comp of chewing gum base - 172.615

grapes to raisins -172.270

Sulfathiazole (Combined w/Chlortetracycline and Penicillin) - FEED, REG, 0.1 ppm neg residue - In uncooked edible tissues of swine - 556.690; Uses in swine feeds - 558.155

Sulfiting agents - PRES, GRAS, GMP, X-ref wi individual sulfiting agents - 182.3616, 182.3637, 182.3739, 182.3766, 182.3798, 182.3862

Sulfomyxin (N-sulfomethylpolymyxin B-Sodium salt) -VET, REG, ZERO - In edible tissues of chickens & turkeys - 556.700;Use - 522.2340

Sulfonated lignin, primarily as calcium & sodium salts - SP/ADJ, REG, GMP, X-ref - Calcium lignosulfonate -573.600; < 4% of finished pellets, of flake grain or fin feed Pelleting aid, binding aid, of flake grain, source of metabolizable energy in finished feed; < 11% molasses - Surfactant in molasses used in feeds

Sulfonated 9-octadecanoic acid - SANI, REG, 156-312 ppm - Comp of sanitizing sln - Followed by adequate draining - 178.1010

Sulfonated oleic acid, Na salt - SANI, REG, GMP, Comp of sanitizing sln - Followed by adequate draining - 178.1010

Sulfur dioxide - PRES, GRAS/FS, Not in meats or in foods recognized as a source of Vitamin B1, etc. (See REG) - 182.3862; BL, REG, < 0.05% - Food starch modifier - 172.892; FUNG, REG, 10.0 ppm - As residues in/on grapes -40 CFR 180.444

Sulfuric acid - MISC, GRAS, GMP - 184.1095; In animal feeds -582.1095; REG, GMP, Food starch modifier -172.892; REG, Manufacture of modified hop extract -172.560; REG, Manufacture of sodium methyl sulfate -173.385; SANI, REG, GMP, Comp of sanitizing sln -Followed by adequate drainage - 178.1010

Synthetic fatty alcohols - MISC, REG, GMP, See Fatty Alcohols, synthetic - 172.864

Synthetic flavoring substances - SY/FL, REG, GMP, See 172.515 for listing and adjuvants

Synthetic glycerin - MISC, REG, GMP, In food - 172.866 for specs

Synthetic isoparaffinic petroleum hydrocarbons -MISC, REG, GMP - 172.882

Synthetic paraffin & succinic derivatives - CTG, REG, GMP, Ctg on fresh citrus, muskmelons, and sweet potatoes

-172.275

T

Tagetes (marigold) oil - FL/ADJ, REG, GMP, As oil only -172.510

Talc - GRAS - 182.2437 (magnesium silicate)

Tall oil rosin, glycerol ester of - MISC, REG, GMP, Softener for chewing gum - 172.615

Tallow alcohol, hydrogenated - AF, REG, GMP, Comp of defoaming agent - 173.340

Tallow, fatty acids - MISC, REG, GMP, In foods - 172.860

Tallow, hydrogenated, oxidized or sulfated - AF, REG, GMP, X-ref - Comp of defoaming agent - 173.340

Tamarind - ESO, GRAS - 182.20

Tangerine - ESO, GRAS - 182.20

Tannic acid - ESO, GRAS; NAT/FL/ADJ, GRAS, See REG, < .01% Baked Goods & Baking Mixes; < .015% - Alc bevs.; < .005% - Nonalc bevs.; < .04% - Froz dairy desserts &

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Regulatory Information
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Regulatory Information for Tall oil

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International Regulatory Status

Worldwide Registration Click on link at right to view registration information for different countries -->	Worldwide Registration for: Tall oil Number of countries where this chemical is: Banned, Restricted or Cancelled: 0 Not legal for import: 0
UNEP Persistent Organic Pollutant (POP)	Not Listed
UNEP Prior Informed Consent Chemical (PIC)	Not Listed
WHO Obsolete Pesticide	Not Listed

U.S. and California Regulatory Status

U.S. EPA Registered	No
U.S. EPA Hazardous Air Pollutant	Not Listed
U.S. EPA Minimum Risk Pesticide (25b list)	No
→ CA Registered	Yes
CA Groundwater Contaminant	Not Listed
CA Toxic Air Contaminant	Not Listed

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Actively Registered AI's by Common Name

There are 975 active AI's
There are 13191 active products

DPR Code	# Products	Common Name
05825	1	(3S, 6R)-3-METHYL-6-ISOPROPENYL-9-DECEN-1-YL ACETATE
05826	1	(3S, 6S)-3-METHYL-6-ISOPROPENYL-9-DECEN-1-YL ACETATE
02199	5	(E)-4-TRIDECEN-1-YL-ACETATE
05315	1	(E)-5-DECEN-1-OL
03974	7	(E)-5-DECENOL
03975	8	(E)-5-DECENYL ACETATE
05966	3	(E,E)-9, 11-TETRADECADIEN-1-YL ACETATE
03866	8	(S)-CYPERMETHRIN
03936	1	(S)-KINOPRENE
05316	3	(Z)-11-HEXADECEN-1-YL ACETATE
02126	4	(Z)-11-HEXADECENAL
02200	5	(Z)-4-TRIDECEN-1-YL-ACETATE
02142	1	(Z)-9-DODECENYL ACETATE
01997	2	(Z,E)-7,11-HEXADECADIEN-1-YL ACETATE
05314	4	(Z,Z)-11,13-HEXADECADIENAL
01998	2	(Z,Z)-7,11-HEXADECADIEN-1-YL ACETATE
02302	2	([([(2-DIHYDRO-5-METHYL-3(2H)-OXAZOLYL)-1-METHYLETHOXY]ME
01893	43	1,2-BENZISOTHIAZOLIN-3-ONE
02313	6	1,2-DIBROMO-2,4-DICYANOBUTANE
02298	10	1,3-BIS(HYDROXYMETHYL)-5,5-DIMETHYL HYDANTOIN
04036	11	1,3-DIBROMO-5,5-DIMETHYLHYDANTOIN
00037	40	1,3-DICHLORO-5,5-DIMETHYLHYDANTOIN

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02870	2	SORBITAN MONOOLEATE
02872	1	SORBITAN TRIOLEATE
01629	3	SORBITOL
01882	1	SOYBEAN FATTY ACIDS, DIMETHYLAMINE SALT
02335	6	SOYBEAN OIL
05946	5	SPINETORAM
03983	24	SPINOSAD
05857	1	SPIRODICLOFEN
05858	5	SPIROMESIFEN
05955	1	SPIROTETRAMAT
03937	2	STREPTOMYCES GRISEOVIRIDIS STRAIN K61
05891	3	STREPTOMYCES LYDICUS WYEC 108
03834	5	STREPTOMYCIN SULFATE
00554	16	STRYCHNINE
03457	1	STYRENE ACRYLIC COPOLYMER
05399	2	STYRENE BUTADIENE COPOLYMER
05230	3	SUCROSE OCTANOATE
00708	5	SUGAR
05923	18	SULFENTRAZONE
02314	10	SULFLURAMID
02149	9	SULFOMETURON-METHYL
01674	1	SULFONATED OLEIC ACID, SODIUM SALT
05136	2	SULFOSULFURON
00560	87	SULFUR
00561	2	SULFUR DIOXIDE
00442	12	SULFURIC ACID
00618	4	SULFURYL FLUORIDE
→ 02912	9	TALL OIL
01389	26	TALL OIL FATTY ACIDS
02155	4	TARTRAZINE
02195	6	TAU-FLUVALINATE
00971	29	TCMTB
03850	32	TEBUCONAZOLE

attachment 9, section 3
page 4/7

PAN Pesticides Database - Pesticide Registration Status

Regulatory Information for Tall oil use in Philippines

Registered for Use:	Yes
Banned or Restricted:	
Consent to Import:	
Notes:	
Source:	Philippines Registered AIs, 1999 . PAN last checked the currency of this data set on 1999.

attachment 9, section 3, page 5/7

PAN Pesticides Database - Pesticide Registration Status

Home > Country Registration
Help | Feedback

Tall oil - Registration, import consent and bans

Note: See Working with the Information on this Page section below for important notes about this data.

Chemical ID	Identifying information for this chemical, including synonyms, ID numbers, use type, and chemical classification.
Summary Toxicity	Summary toxicity to humans, including carcinogenicity, reproductive and developmental toxicity, neurotoxicity, and acute toxicity.
International Registration	Information on the status of this pesticide as legally registered for use, banned, cancelled or severely restricted for countries for which PAN has data.

Basic Chemical Information for Tall oil

Top ⬆

For detailed chemical information see the chemical detail page.

Basic Identification Information About This Chemical

Chemical Name	Tall oil
CAS Number	8002-26-4
U.S. EPA PC Code	067211
CA DPR Chem Code	2912
Use Type	Adjuvant
Chem Class	Botanical

Synonyms

Chemical versus Common Names

02912 (CA DPR Chem Code) , 067211 (US EPA PC Code) , 2912 (CA DPR Chem Code) , 8002-26-4 (CAS Number) , 8002264 , 8002264 (CAS Number) , Tall , Tall oil , Talloil

Summary Toxicity Information for Tall oil

Top ⬆

For detailed chemical information see the chemical detail page.

Note: Information for many chemicals is incomplete and may not be fully representative of effects on humans. Why?

Summary Toxicity Information

PAN Bad Actor Chemical [1]	Acute Toxicity [2]	Carcinogen	Cholinesterase Inhibitor	Ground Water Contaminant	Developmental or Reproductive Toxin	Endocrine Disruptor
Not Listed	?	?	No	?	?	?

☠	Indicates high toxicity in the given toxicological category.
?	Indicates no available weight-of-the-evidence summary assessment. For additional information on toxicity from scientific journals or registration documents, see the "Additional Resources for Toxicity " section of the chemical detail page.

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1. **PAN Bad Actors** are chemicals that are one or more of the following: highly acutely toxic, cholinesterase inhibitor, known/probable carcinogen, known groundwater pollutant or known reproductive or developmental toxicant. NOTE! Because there are no authoritative lists of Endocrine Disrupting (ED) chemicals, EDs are not yet considered PAN Bad Actor chemicals.

2. The acute toxicity reported on this page is of the pure chemical ingredient only and may not reflect the acute toxicity of individual pesticide products. To view acute toxicity of individual products, click on 'View Products' link in the 'Chemical Identification' section above.

International Registration Information for Tall oil

Top

International Regulatory Status

UNEP Persistent Organic Pollutant (POP)	Not Listed
UNEP Prior Informed Consent Chemical (PIC)	Not Listed
WHO Obsolete Pesticide	Not Listed
WHO Acute Hazard Ranking	Not Listed

Summary of Regulatory Status

Of the countries we have data for, the chemical is:

Banned or Restricted in:	0 Countries
Illegal to Import into:	0 Countries Countries

Africa Region

Country	Registered for Use	Banned or Restricted	Consent to Import	Notes and References
Burkina Faso	No			Notes
Cameroon	No			Notes
Cape Verde	No			Notes
Chad	No			Notes
Gambia	No			Notes
Madagascar	No			Notes
Niger	No			Notes
Tanzania	No			Notes
Uganda	No			Notes

Asia and the Pacific Region

Country	Registered for Use	Banned or Restricted	Consent to Import	Notes and References
Australia	No			Notes
India	No			Notes
New Zealand	No			Notes
Philippines	Yes			Notes

attachment 9, section 3
page 7/7

Europe and Central Asia Region

Country	Registered for Use	Banned or Restricted	Consent to Import	Notes and References
📖 Denmark	No			📖 Notes
📖 Finland	No			📖 Notes
📖 Germany	No			📖 Notes
📖 Hungary	No			📖 Notes
📖 Netherlands	No			📖 Notes
📖 Portugal	No			📖 Notes
📖 United Kingdom	No			📖 Notes

North America Region

Country	Registered for Use	Banned or Restricted	Consent to Import	Notes and References
📖 Canada	No			📖 Notes
📖 United States	No			📖 Notes

Working with the Information on this Page

Click on underlined terms for definitions or go to the Pesticide Tutorial overview page.

Any underlined term with a book icon 📖 has additional information.

To print this page, choose **Print**. To export this data, choose **Save As** 'HTML Source' and open it in Excel or equivalent program.

Entries are listed in **red** when the chemical is either: a) not registered for use; b) banned or severely restricted or; c) it is illegal to import the chemical into the country.

Citation: Kegley, S.E., Hill, B.R., Orme S., Choi A.H., *PAN Pesticide Database*, Pesticide Action Network, North America (San Francisco, CA, 2008), http://www.pesticideinfo.org.

SANCO DOC 3010 - Directive 91/414/EEC

attachment 10, section 3 page 1/2

Registration as a repelent

1179 Substances (936 exist, 99 other, 144new)	Cipac	Category	List	Annex I 91/414	Legislation	Remarks	#	RMS	Assess Risk?	MRLs 'Trade'	MRLs Cereal	MRLs Animal	MRLs Plant
Repellents: Tall oil crude (CAS 8002-26-4) (by smell)			4A	pending		Animal pro	80	EL	EFSA				
Repellents: Tall oil pitch (CAS 8016-81-7) (by smell)			4A	pending		Animal pro	81	EL	EFSA				
Sea-algae extract		PG	4A	pending		Plant extract	82	IT	EFSA				
Seaweed			4A	pending		Plant extract	83	IT	EFSA				
Sodium aluminium silicate		RE	4A	pending			84	HU	EFSA				
Sodium hypochlorite		BA	4F	pending		Disinfectant	85	NL	EFSA				
Sulphur	18	FU, AC, RE	4A	pending		Commodity	86	FR	EFSA				
Sulphuric acid		HB	4A	pending		Commodity	87	FR	EFSA				
Trimethylamine hydrochloride			4A	pending		Commodity	88	BE	EFSA				
Urea		IN	4A	pending		Food/feed	89	EL	EFSA				
Zinc phosphide (incl. Phosphine)	69	RO	4D	pending		Rodenticide	90	DE	EFSA		86/362		

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SANCO 3010

The list of active substances is divided in 3 main categories:

- **A** **Old** (existing) active substances (i.e. substances on the market before 1993)
- **B** Substances **not considered in the scope** of directive 91/4141/EEC (either because already banned or never notified under Dir. 91/414/EEC or becaus
- **C** **New** active substances (i.e. substances on the market after 1993)

Old active substances are divided in 4 lists (or stages), defined according to directive 91/414 (see column F)

Each category shows **3 different colours**:
GREEN: substances included in annex I to directive 91/414/EEC, and that therefore can be authorised in the EU
ORANGE: substances not included in annex I to directive 91/414/EEC, and that therefore cannot be authorised in the EU
YELLOW: substances for which the evaluation is still on-going. Pending any decision, they can be authorised in the EU.

Section 4 List of Attachments

No Attachments

Section 5 List of Attachments

Attachment 1, section 5: process, Wikipedia
Attachment 2, section 5: Tall oil Life Cycle (Forchem)

Attachment 3, section 5: Fractionation of the tall oil (Forchem)-for crude tall oil

Attachment 4, section 5: Fractionation of Crude tall oil (Forchem)-description letter provided by Quality Manager of Forchem Tall Oil Refinery in Rauma, Finland.

Attachment 5, section 5: Production chain Forchem for crude tall oil;

Attachment 6, section 5: Full tall oil scheme of the technological process (manufacturing process in Finnish);

Attachment 7, section 5: Figure 1-Tall oil Process Forestry Tall Oil

attachment 1, section 5

Kraft process

From Wikipedia, the free encyclopedia

The **Kraft process** (also known as **Kraft pulping** or **sulfate process**) describes a technology for conversion of wood into wood pulp consisting of almost pure cellulose fibers. The process entails treatment of wood chips with a mixture of sodium hydroxide and sodium sulfide that break the bonds that link lignin to the cellulose. The process name is derived from German *kraft*, meaning *strength/power*; both capitalized and lowercase names (*Kraft process* and *kraft process*) appear in the literature, but "kraft" is most commonly used in the pulp and paper industry.

Contents

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History

The kraft process was developed by Carl F. Dahl in 1879, and a pulp mill using this technology started (in Sweden) in 1890.[1] The invention of the recovery boiler by G.H. Tomlinson in the early 1930s, was a milestone in the advancement of the kraft process.[2] It enabled the recovery and reuse of the inorganic pulping chemicals such that a kraft mill is almost closed-cycle with respect to inorganic chemicals, apart from those used in the bleaching process. For this reason, in the 1940s, the kraft process surpassed the sulfite process as the dominant method for producing wood pulp.[1]

The process

Wood chips are fed into vessels called digesters that are capable of withstanding high pressures. Some digesters operate in a batch manner and some in a continuous process, such as the Kamyr digester. Digesters producing 1,000 tonnes of pulp per day and more are common.[3]


International Paper: Kraft paper mill

Wood chips and **white liquor**, a mixture of sodium hydroxide and sodium sulfide, produced in the recovery process, are added to the top of the digester. In a continuous digester the materials are fed at a rate which allows the pulping reaction to be complete by the time the material exit the reactor. Typically delignification requires several hours at 130 to 180 °C (265 to 355 °F). Under these conditions lignin and some hemicellulose degrade to give fragments that are soluble in the strongly basic liquid. The solid pulp (about 50% by weight based on the dry wood chips) is collected and washed. At this point the pulp is quite brown and is

Attachment 1, section 5:

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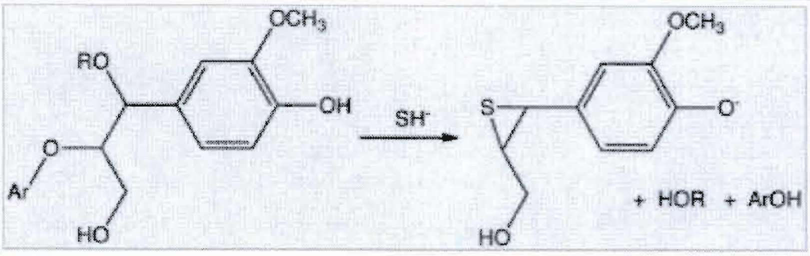
known as "brown stock". The combined liquids, known as black liquor (so called because of its color), contain lignin fragments, carbohydrates from the breakdown of hemicellulose, sodium carbonate, sodium sulfate and other inorganic salts.

One of the main chemical reactions that underpin the kraft process is the scission of ether bonds by the nucleophilic sulfide (S^{2-}) or bisulfide (HS^-) ions.[2]



net reaction in depolymerization of lignin by SH^- (Ar = aryl, R = alkyl groups).

Recovery process

The black liquor is concentrated in multiple effect evaporator to 60% or even 80% solids ("heavy black liquor"[4]) and burned in the recovery boiler to recover the inorganic chemicals for reuse in the pulping process. Higher solids in the concentrated black liquor increases the energy and chemical efficiency of the recovery cycle, but also gives higher viscosity and precipitation of solids (plugging and fouling of equipment).[5][6] The combustion is carried out such that sodium sulfate is reduced to sodium sulfide by the organic carbon in the mixture:

1. $Na_2SO_4 + 2\ C \rightarrow Na_2S + 2\ CO_2$

This reaction is similar to Thermo Chemical Sulfato Reduction (TSR) in geochemistry.

The molten salts ("smelt") from the recovery boiler are dissolved in a process water known as weak wash. This process water also known as weak white liquor is composed of all liquors used to wash lime mud and green liquor precipitates and is kept in a tank called weak wash storage tank. The solution of sodium carbonate and sodium sulfide resulted is known as "green liquor". This liquid is mixed with calcium hydroxide to regenerate the white liquor used in the pulping process through an equilibrium reaction (Na_2S is shown since it is part of the green liquor, but does not participate in the reaction):

2. $Na_2S + 2\ Na_2CO_3 + Ca(OH)_2 \longleftrightarrow Na_2S + 2\ NaOH + CaCO_3$

Calcium carbonate precipitates from the white liquor and is recovered and heated in a lime kiln where it is converted to calcium oxide (lime).

3. $CaCO_3 \rightarrow CaO + CO_2$

Calcium oxide (lime) is reacted with water to regenerate the calcium hydroxide used in Reaction 2:

4. $CaO + H_2O \rightarrow Ca(OH)_2$

The combination of reactions 1 through 4 form a closed cycle with respect to sodium, sulfur and calcium and is the main concept of the called recausticizing process where sodium carbonate is reacted to regenerate sodium hydroxide.

The recovery boiler also generates high pressure steam which is led to turbogenerators, reducing the steam pressure for the mill use and generating electricity. A modern kraft pulp mill is more than self-sufficient in its electrical generation and normally will provide a net flow of energy to the local electrical grid.[7] Additionally, bark and wood residues are often burned in a separate power boiler to generate steam.

Comparison with other pulping processes

Pulp produced by the kraft process is stronger than that made by other pulping processes. Acidic sulfite processes degrade cellulose more than the kraft process, which leads to weaker fibers. Kraft pulping removes most of the lignin present originally in the wood whereas mechanical pulping processes leave most of the lignin in the fibers. The hydrophobic nature of lignin[8] interferes with the formation of the hydrogen bonds between cellulose (and hemicellulose) in the fibers needed for the strength of paper[1] (strength refers to tensile strength and resistance to tearing).

Kraft pulp is darker than other wood pulps, but it can be bleached to make very white pulp. Fully bleached kraft pulp is used to make high quality paper where strength, whiteness and resistance to yellowing are important.

The kraft process can use a wider range of fiber sources than most other pulping processes. All types of wood, including very resinous types like southern pine[9], and non-wood species like bamboo and kenaf can be used in the kraft process.

Bleaching

In a modern mill, brownstock (cellulose fibers containing approximately 5% residual lignin), produced by the pulping is first washed to remove some of the dissolved organic material and then further delignified by a variety of bleaching stages.[10]

In the case of a plant designed to produce pulp to make brown sack paper or linerboard for boxes and packaging, the pulp does not always need to be bleached to a high brightness. Bleaching decreases the mass of pulp produced by about 5%, decreases the strength of the fibers and adds to the cost of manufacture.

Byproducts and emissions

In the case of softwood (conifer) pulping, a soaplike substance is collected from the liquor during evaporation. The soap is acidified to produce tall oil, a source of resin acids, fatty acids and other chemicals. Also turpentine originates from softwood.

Various byproducts containing hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and other volatile sulfur compounds are the cause of the malodorous air emissions characteristic for pulp mills utilizing the kraft process. Outside the modern mills the odour is perceivable only during disturbance situations, for example when shutting the mill down for maintenance break. This is due to practiced collection and burning of these odorous gases in the recovery boiler along with black liquor. The sulfur dioxide emissions of the kraft pulp mills are much lower than sulfur dioxide emissions from sulfite mills. In modern mills where high dry solids are burned in the recovery boiler hardly any sulfur dioxide leaves the boiler. This is mainly due to higher lower furnace temperature which leads to higher sodium release from the black liquor droplets that can react with sulfur dioxide forming sodium sulfate.

The process effluents are treated in a biological effluent treatment plant, which guarantees that the effluents are not toxic in the recipient.

See also

- Sulfite process
- Pulp mill
- Wood pulp
- Bleaching of wood pulp
- Paper

References

1. ^ a b c Biermann, Christopher J. (1993). *Essentials of Pulping and Papermaking*. San Diego: Academic Press, Inc.. ISBN 0-12-097360-X.
2. ^ a b E. Sjöström (1993). *Wood Chemistry: Fundamentals and Applications*. Academic Press.
3. ^ Woodman, Jocelyn (1993). "[1] (http://www.p2pays.org/ref\02\01128/01128.pdf) Pollution Prevention Technologies for the Bleached Kraft Segment of the U.S. Pulp and Paper Industry (see p 66)]". U.S. Environmental Protection Agency. Retrieved on 2007-09-11.
4. ^ "Equipment to handle heavy black liquor (http://www.sealspecialists.net/black%20liquor.htm)". Retrieved on 2007-10-09.
5. ^ Hsieh, Jeffery S.; Smith, Jason B.. "Second Critical Solids Black Liquor Scaling (http://thor.lib.chalmers.se/inst_fack/kurser/keml/TK/materials/dc220.pdf)". Pulp and Paper Engineering, School of Chemical Engineering, Georgia Institute of Technology. Retrieved on 2007-10-09.
6. ^ US patent 5527427 (http://v3.espacenet.com/textdoc?DB=EPODOC&IDX=US5527427), *"High solids black liquor of reduced viscosity and viscosity reduction method for high solids black liquor"*, granted 1996-06-18, assigned to Optima Specialty Chemicals & Technology Inc
7. ^ Jeffries, Tom (March 27, 1997). "Kraft pulping: Energy consumption and production (http://www2.biotech.wisc.edu/jeffries/bioprocessing/pulping.html)". University of Wisconsin Biotech Center [2] (http://www.biotech.wisc.edu/). Retrieved on 2007-10-21.
8. ^ Hubbe, Martin a.; Lucian A. Lucia (2007). "The "Love-Hate" Relationship Present in Lignocellulosic Materials (http://www.bioresourcesjournal.com/article/view/BioRes_2_4_534_535_Hubbe_Lucia_Love_and_Hate_Lignocellulosics/932)" (). *BioResources* **2** (4): 534–535. Retrieved on 2007-09-15.
9. ^ "The Southern Pines (http://www.fpl.fs.fed.us/documnts/usda/amwood/256spine.pdf)". US Department of Agriculture (1985). Retrieved on 2007-09-13.
10. ^ "Environmental Comparison of Bleached Kraft Pulp ManufacturingTechnologies (http://www.environmentaldefense.org/pdf.cfm?ContentID=1626&FileName=WP5.pdf)". Retrieved on 2007-09-28.

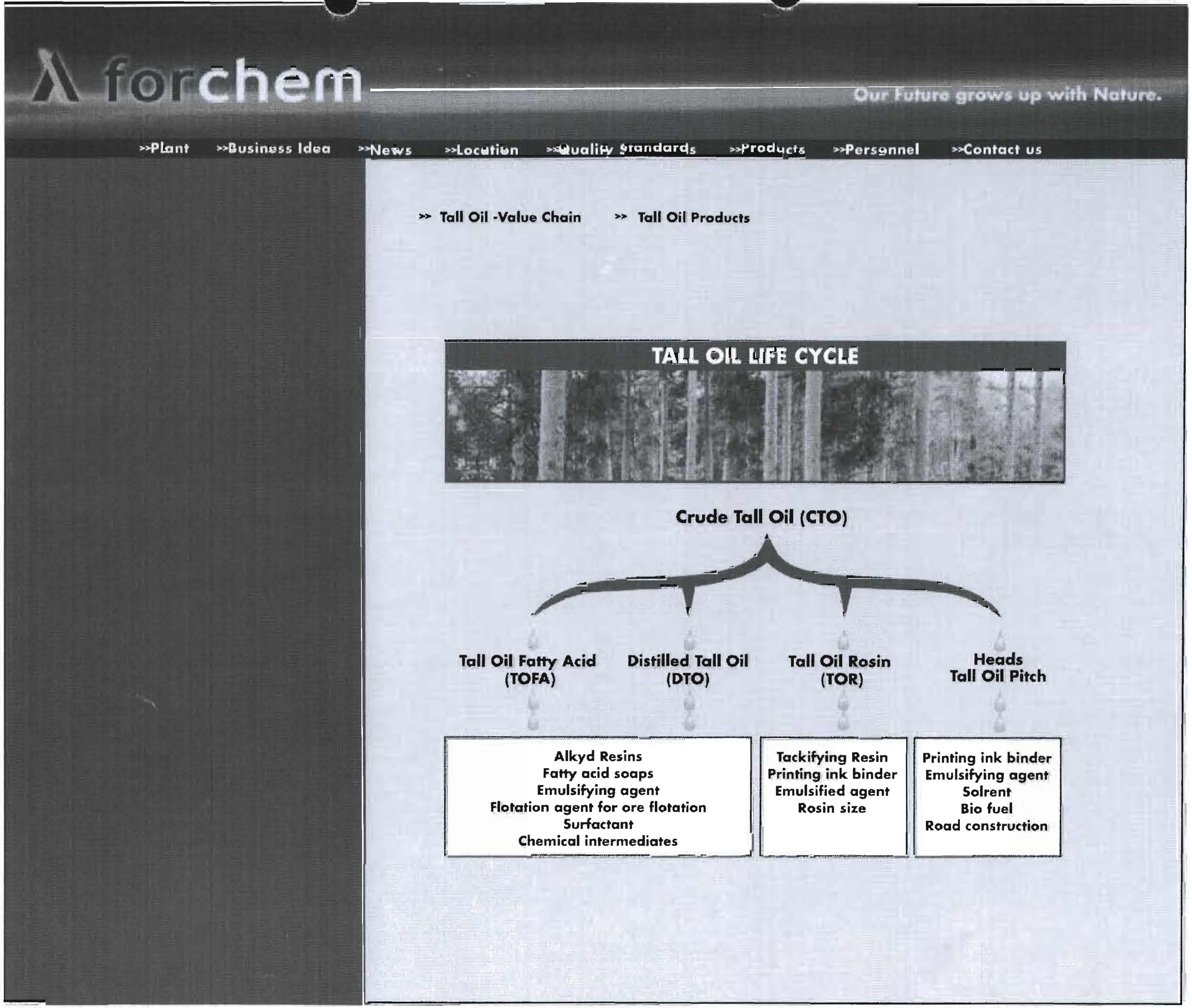
External links

- US EPA article on Kraft pulping (http://www.epa.gov/ttn/chief/ap42/ch10/final/c10s02.pdf)
- Reference Document on Best Available Techniques in Pulp and Paper Industry by European Commission, 2001 (http://eippcb.jrc.es/pages/FActivities.htm)

Retrieved from "http://en.wikipedia.org/wiki/Kraft_process"
Categories: Industrial processes | Pulp and paper industry
Hidden categories: All articles with dead external links | Articles with dead external links since May 2008

- This page was last modified on 22 September 2008, at 00:52.
-

Attachment 2, section : Tall oil life cicle (Forchem)



forchem

Our Future grows up with Nature.

>>Plant >>Business Idea >>News >>Location >>Quality Standards >>Products >>Personnel >>Contact us

>> Tall Oil -Value Chain >> Tall Oil Products

TALL OIL LIFE CYCLE

Crude Tall Oil (CTO)

Tall Oil Fatty Acid (TOFA)

- Alkyd Resins
- Fatty acid soaps
- Emulsifying agent
- Flotation agent for ore flotation
- Surfactant
- Chemical intermediates

Distilled Tall Oil (DTO)

Tall Oil Rosin (TOR)

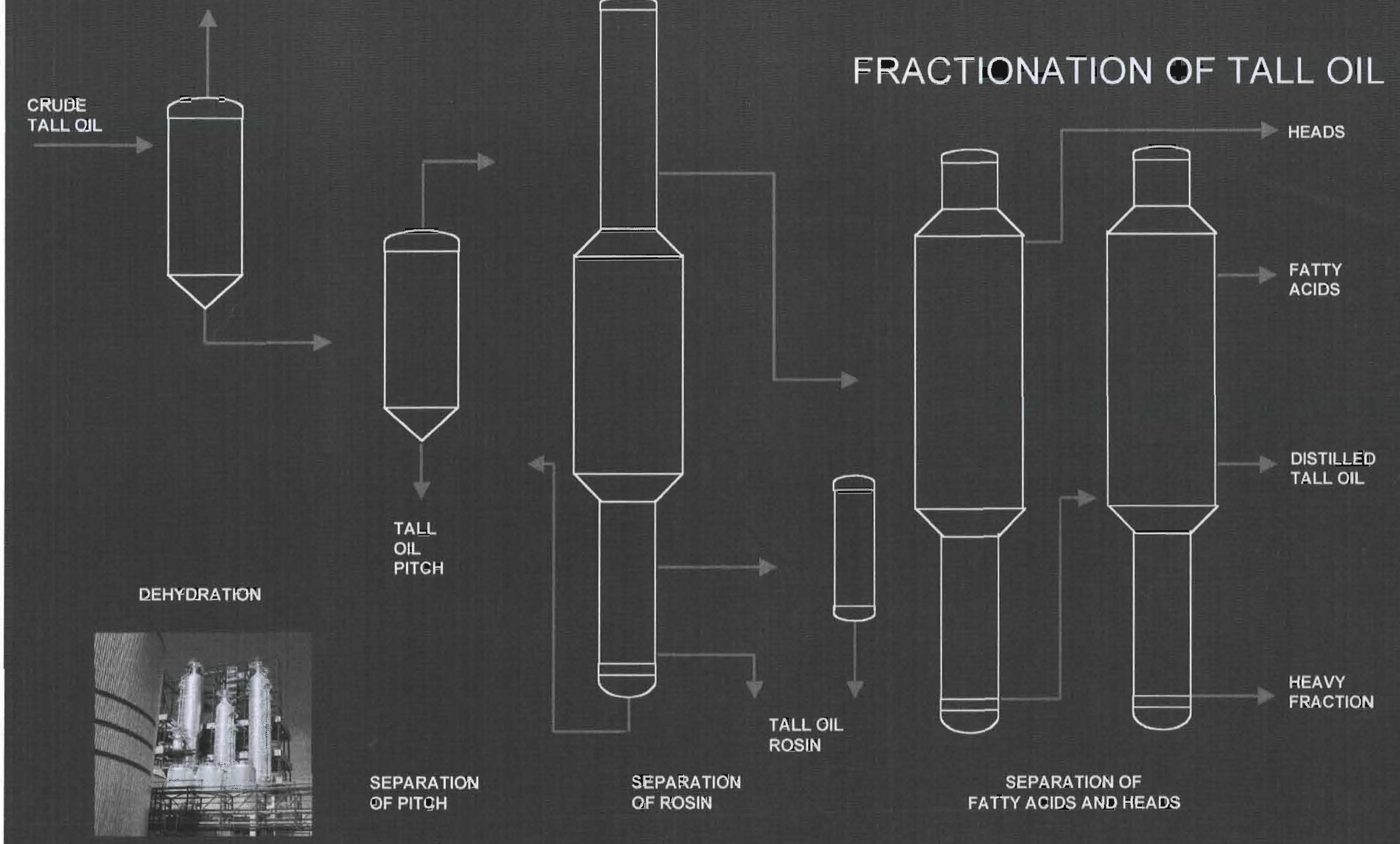
- Tackifying Resin
- Printing ink binder
- Emulsified agent
- Rosin size

Heads
Tall Oil Pitch

- Printing ink binder
- Emulsifying agent
- Solrent
- Bio fuel
- Road construction

Attachment 3, section 5
Fractionation of crude tall

FRACTIONATION OF TALL OIL



CRUDE TALL OIL

DEHYDRATION

TALL OIL PITCH

SEPARATION OF PITCH

SEPARATION OF ROSIN

TALL OIL ROSIN

HEADS

FATTY ACIDS

DISTILLED TALL OIL

HEAVY FRACTION

SEPARATION OF FATTY ACIDS AND HEADS

forchem

Attachment 4, section 5
Fractionation of Crude tall oil

Our future grows up with Nature.

Rauma 13th November 2008

Fractional distillation of Crude Tall Oil

This is simple description of fractional distillation of Crude Tall Oil (CTO) taken place in state of the art facilities of Forchem Tall Oil refinery in Rauma, Finland.

CTO is a complex mixture derived from mostly pine tree originated extractives. CTO consist mostly tall oil fatty acids and tall oil rosin acids. Fractional distillation can be divided into 7 main stages of process:

1. Dehydration of CTO
2. Pitch separation from CTO
3. Rosin separation from CTO
4. Heads separation from CTO
5. Fatty acids separation of CTO
6. Distilled Tall Oil separation of CTO
7. Heavy fraction separation and utilization for energy

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Separation of different fractions is based on their different physical properties. This means fractions boiling in different temperatures and pressures are collected separately. Accurate information of boiling points and pressures used in our process are considered as confidential.

All the stages are carefully monitored by On-Line temperature and pressure measurements. Also QC samples for normal laboratory analyses are taken daily to ensure processes capability to produce high quality products.

All the end products are analyzed before shipping them to customers and also retain samples are collected.

FORCHEM OY

Mikkko Rintola, Quality Manager

forchem

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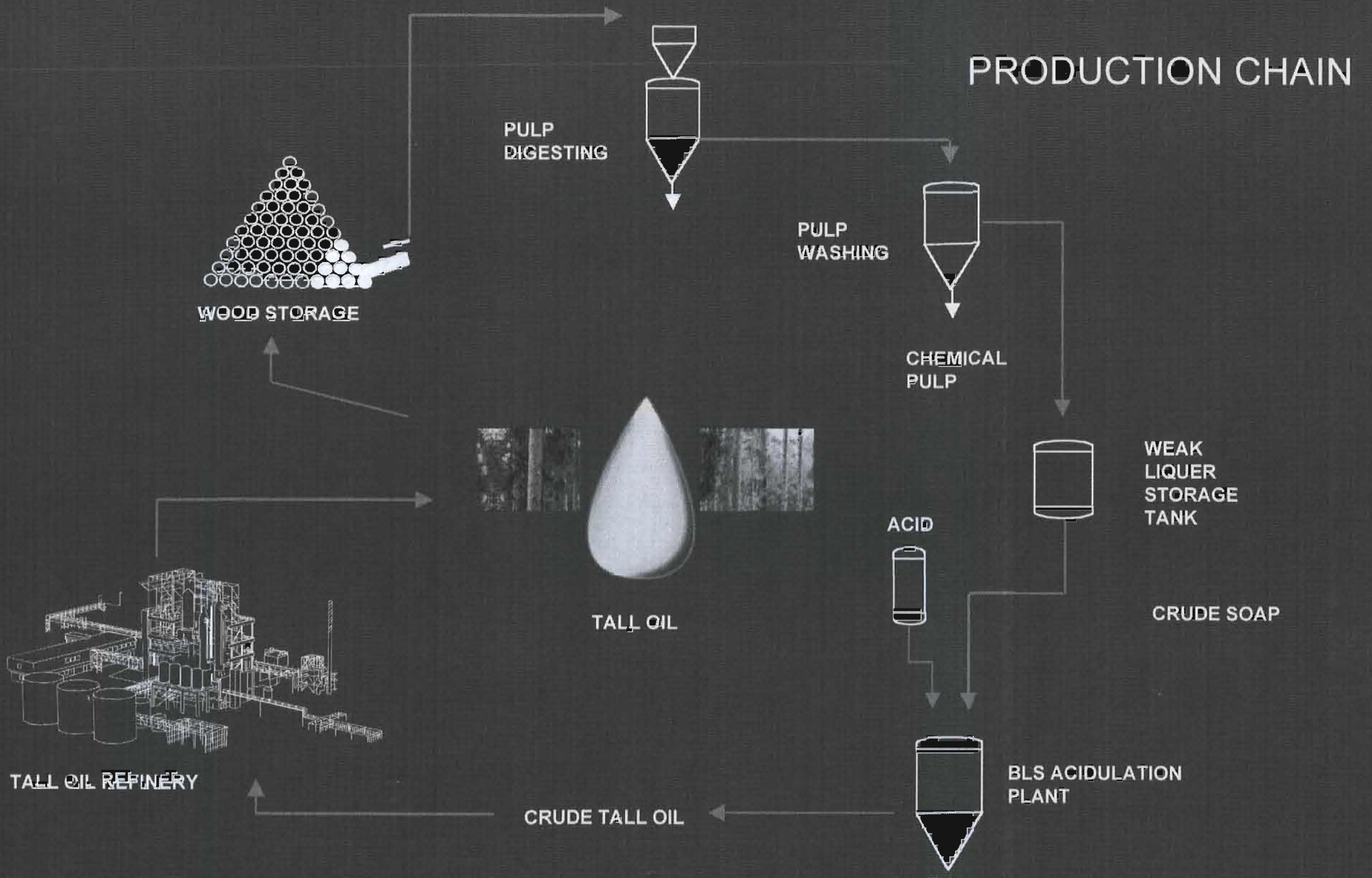
fax +358 2 478 4499
Business ID 1614382-3
VAT ID nro FI16143823

Attachment 5, section 5
Production Chain Forchem for crude tall oil

DEC 15 2008

PRODUCTION CHAIN



WOOD STORAGE

PULP DIGESTING

PULP WASHING

CHEMICAL PULP

WEAK LIQUER STORAGE TANK

CRUDE SOAP

ACID

BLS ACIDULATION PLANT

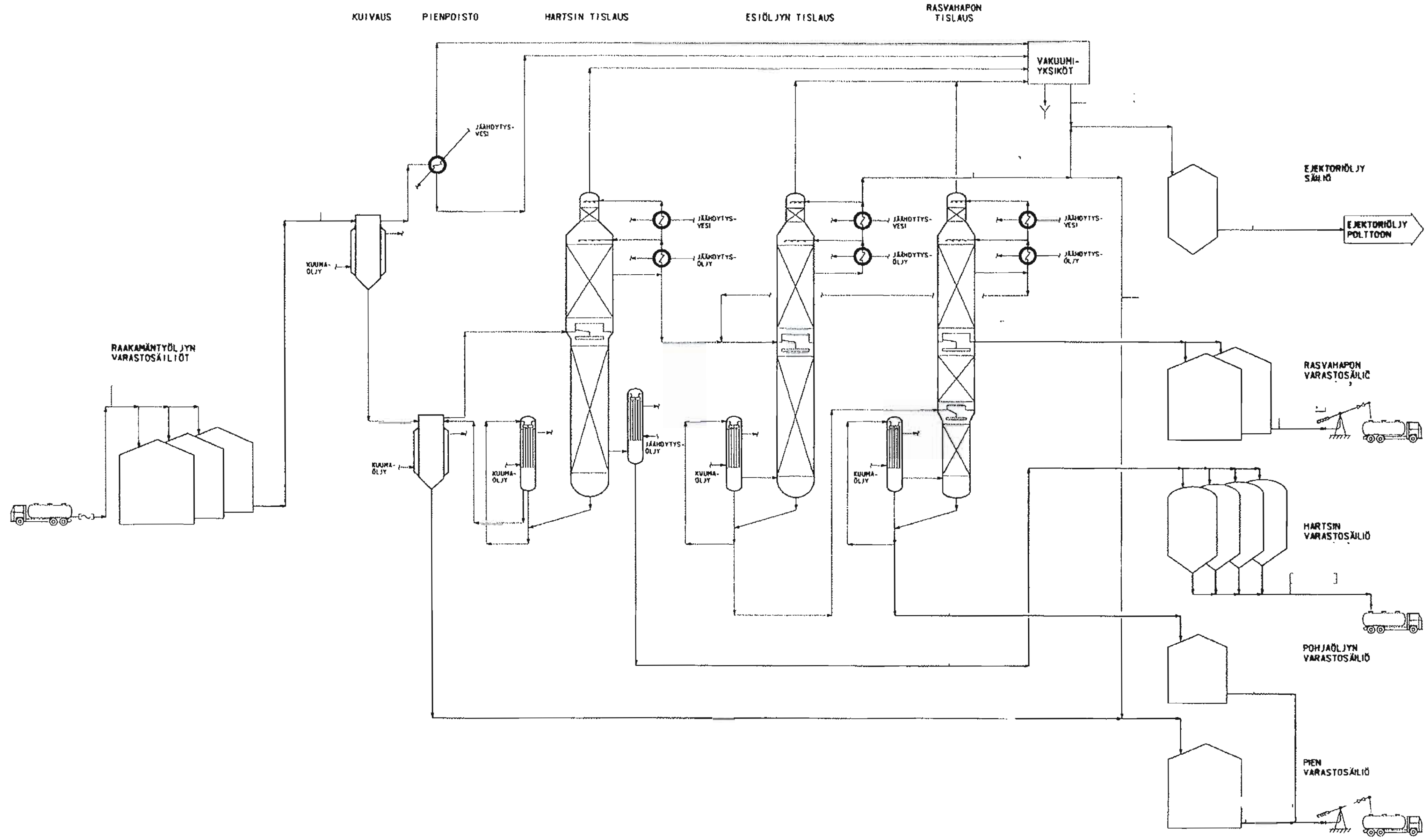
CRUDE TALL OIL

TALL OIL REFINERY

TALL OIL

forchem

attachment 6 section 5 Full tall oil scheme of the technological process



Attachment 7, section 5

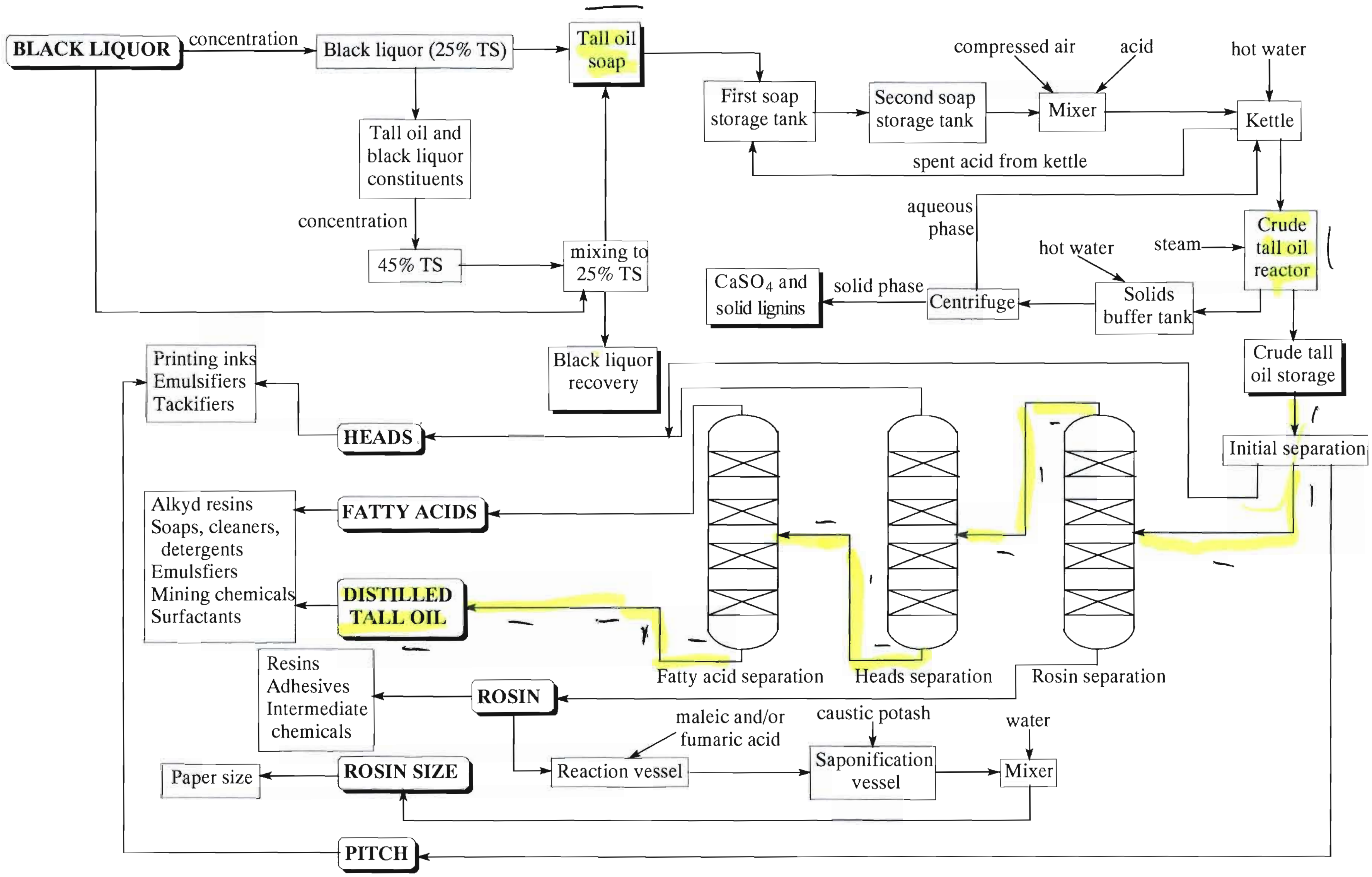


Figure 1 - The tall oil process

Section 6 List of Attachments

No Attachments

Section 7 List of Attachments

Attachment 1, section 7: Initial Risk-Based Prioritization of High Production Volume Chemicals, September 2008

Attachment 2, section 7: e-CFR Title 40: Protection from the Environment, exemptions from tolerances, 2.10.2008

Attachment 3, section 7: Methyl Esters of Tall-Oil Fatty Acids; Tolerance Exemption EPA 40 CFR Part 18

Attachment 4, section 7: list 3 of inert ingredients in the EPA

Attachment 5, section 7: Food additive status list

Attachment 6, section 7: Europe; existing active substances; SANCO DOC 3010

Attachment 7, section 7: Agency Response letter GRAS Notice No GRN 00039

Attachment 8, section 7: Application A417-Tall oil non-esterified phytosteols derived from tall oil, Full assessment, 10 October 2001

Attachment 9, section 7 includes the following references:

- Substances in Cosmetics and Personal Care Products regulated under the Food and Drugs Act (F& DA) .
- PMRA Consolidated list formulants sorted by CAS Number.
- U.S. Environmental Protection Agency, List of inert Pesticide Ingredients.
- PAN Pesticide Database – Pesticide Registration Status

Attachment 1, section 7.

DEC 15 2008

U.S. Environmental Protection Agency
Risk-Based Prioritization Document

September 2008

Initial Risk-Based Prioritization of High Production Volume Chemicals

Tall Oil and Related Substances Category

Tall oil	**(CASRN 8002-26-4)**
Tall oil, sodium salt	**(CASRN 65997-01-5)**
Tall oil, potassium salt	**(CASRN 68647-71-2)**
Wastewater, tall-oil soap acidulation	**(CASRN 65997-02-6)**
Tall oil, disproportionated	**(CASRN 68152-92-1)**
Tall oil, disproportionated, potassium salt*	**(CASRN 68527-29-7)**
Tall-oil pitch	**(CASRN 8016-81-7)**
Tall-oil pitch, sodium salt	**(CASRN 68140-16-9)**

(*added to the category after the original HPV submission at the sponsor's request because fulfills HPV criteria based on the 2002 IUR)

This document is based on screening-level characterizations done by EPA on the environmental fate, hazard, and exposure of the listed chemicals. The information used by EPA includes data submitted under the HPV Challenge Program[1] and the 2006 Inventory Update Reporting (IUR)[2], and data publicly available through other selected sources[3]. This screening-level prioritization presents EPA's initial thinking regarding the potential risks presented by these chemicals and future possible actions that may be needed. These initial characterization and prioritization documents do not constitute a final Agency determination as to risk, nor do they determine whether sufficient data are available to characterize risk. Rather, they are interim evaluations. Recommended actions may be considered by EPA in the future based on a relative judgment regarding these chemicals in comparison with others evaluated under this program, and in light of the uncertainties presented by gaps in the available data that may be determined to exist. These evaluations contribute to meeting U.S. commitments under the chemicals cooperation work being done in North America[4] through the EPA Chemical Assessment and Management Program (ChAMP)[5].

Hazard and Fate Summary:

- Human Health: Available studies indicate that the acute oral toxicity for several members of this category is low. CASRN 8002-26-4 was selected as representative of this category for testing the remaining endpoints. Repeated oral exposures in animal studies showed low toxicity. There was no developmental toxicity and low reproductive toxicity observed in a combined repeated dose/reproductive/developmental toxicity screening test. CASRN 8002-26-4 did not show mutagenic potential or induce chromosomal effects in *in vitro* tests.
- Environment: Available data indicate that the potential acute hazard to fish, aquatic invertebrates and aquatic plants is low. Based on their environmental fate

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[1] US EPA, HPV Challenge Program information: http://www.epa.gov/hpv/.
[2] US EPA, IUR information: http://www.epa.gov/oppt/iur/index.htm
[3] US EPA, Information on additional public databases used: http://www.epa.gov/hpvis/pubdtsum.htm
[4] US EPA, U.S. Commitments to North American Chemicals Cooperation: http://www.epa.gov/hpv/pubs/general/sppframework.htm
[5] US EPA, ChAMP information: http://www.epa.gov/champ/.

characterization (generally not persistent or bioaccumulative) the hazard to aquatic organisms under chronic exposure conditions is expected to be low for all category members except for CASRN 8016-81-7 and CASRN 68140-16-9. While CASRN 8016-81-7 and CASRN 68140-16-9 are moderately persistent (but not bioaccumulative), they are semi-solid/solid and virtually insoluble in water which is expected to limit chronic toxicity.

- Persistence and Bioaccumulation:
  - Available data indicate that CASRN 8016-81-7 and CASRN 68140-16-9 have moderate persistence. The other chemicals in this category have low persistence.
  - Available data indicate that the chemicals in this category have low bioaccumulation potential.

Exposure Summary:

- Both Confidential Business Information (CBI) and non-confidential information from IUR and other sources were used in developing this initial prioritization.
- Production Volume: The ranges reported below are based on 2006 IUR submissions.
  - Five category members are HPV chemicals:
    - CASRNs 8002-26-4 and 65997-02-6: = 1 billion lbs.
    - CASRN 65997-01-5: = 500 million and < 1 billion lbs.
    - CASRN 8016-81-7: =100 million and < 500 million lbs.
    - CASRN 68140-16-9: = 1 million and < 10 million lbs.
  - Two category members are MPV chemicals:
    - CASRN 68647-71-2: = 0.5 million and < 1 million lbs.
    - CASRN 68152-92-1: < 0.5 million lbs.
  - One category member does not have an IUR submission:
    - CASRN 65997-02-6.
- Uses: Non-confidential information in the IUR indicates that there are 45 manufacturers of crude CASRN 8002-26-4, all of which are paper manufacturers, and fractionators of CASRN 8002-26-4. Most companies and sites use the fractionated product(s) as a reactant or component in formulated products. There may be other companies and sites that are claimed confidential. Six of the eight chemicals in this category have IUR submissions. Non-confidential IUR information indicates a variety of uses for these chemicals including uses as intermediates, flotation agents, fuels, and adhesive and binding agents. All six chemicals have IUR submissions that indicate commercial or consumer uses. Information submitted as part of the HPV Challenge Program also provides information on uses. CASRN 8002-26-4 is used as a feedstock to the fractionation process and separated into rosin, fatty acids, distilled CASRN 8002-26-4, heads, pitch, etc. CASRN 65997-01-5 is used in the production of adhesives and binding agents, flotation agents, pigments, metalworking fluids and lubricants, and soaps and detergents. CASRN 65997-02-6, composed of dilute CASRN 8002-26-4, has no commercial value and is either recycled to the pulping process or diverted to wastewater treatment. CASRN 68140-16-9 is used in the asphalt industry as a bonding agent in paving applications or as a plasticizer in asphalt coatings. CASRN 68152-92-1 is used in the production of rubber and neoprene. CASRN 68647-71-2 is used in the production of soaps and detergents, metal-working fluids and lubricants. CASRN 8016-81-7 is used as a fuel by the CASRN 8002-26-4 processor, and in adhesives. The Hazardous Substances

Data Bank (HSDB) information for CASRN 8002-26-4 lists uses as the manufacturing of soap pastes, flotation agents, greases, paint, rubber formulation, cutting oils and sulfonated oils.

- General Population and Environment: EPA identifies a medium potential that the general population and the environment may be exposed based on information on known uses and environmental fate. There may be potential for environmental releases, although the quantity of releases to various media including water is unknown.
- Workers: EPA identifies a medium relative ranking for potential worker exposure. This relative ranking is based on the relatively non-volatile nature of these chemicals, the relatively high production volume, the industrial processing and use information, the relatively high number of sites, the potential for dermal exposure, and a relatively high number of potentially exposed workers. Members of this category do not have OSHA Permissible Exposure Limits (PELs).
- Consumers: EPA identifies a high potential that consumers may be exposed based on the use of products containing these chemicals. IUR submissions indicate that six of the chemicals have uses in commercial settings or consumer uses such as in paper products, soaps, polishes, and lubricants.
- Children: Based on known uses in products intended for children and that exposures to children may be expected to occur through the household use of some consumer products, EPA identifies a high potential that children might be exposed. Non-confidential IUR information for CASRN 8002-26-4 reported uses in products intended to be used by children. IUR submissions for CASRN 65997-01-5 and CASRN 8016-81-7 reported that such information was Not Readily Obtainable. IUR submissions for CASRN 65997-02-6 reported no uses in products intended to be used by children.

Risk Characterization Summary:

- Potential Risk to Aquatic Organisms from Environmental Releases: *LOW CONCERN*. EPA identifies a medium potential that aquatic organisms might be exposed from environmental releases. All category members have low bioaccumulation potential and six of the eight members have low environmental persistence. These characteristics in combination with the low acute toxicity for fish, invertebrates and aquatic plants, suggest a low concern for potential risk to aquatic organisms.
- Potential Risk to the General Population from Environmental Releases: *LOW CONCERN*. EPA identifies a medium potential that the general population might be exposed from environmental releases. The potential human health hazard is expected to be low due to minimal toxicity in animals following repeated exposures at high doses. Given the low hazard and the environmental fate characteristics of low persistence (for most category members) and low bioaccumulation (all category members), the available information suggest a low concern for potential risk to the general population from environmental releases.
- Potential Risk to Workers: *LOW CONCERN*. EPA identifies a medium relative ranking for potential worker exposure. The potential human health hazard is expected to be low. The available information suggests a low concern for potential risks to workers.
- Potential Risk to Consumers from Known Uses: *LOW CONCERN*. EPA identifies a high potential that consumers may be exposed. The potential human health hazard is

expected to be low. The available information suggests a low concern for potential risks to consumers.

- Potential Risk to Children: *LOW CONCERN*. EPA identifies a high potential that children may be exposed. Uses in products specifically intended to be used by children were reported in the IUR for some category members. Exposures to children may also be expected to occur through the household use of some consumer products. Available toxicity data exist with animals exposed postnatally and no toxicity was observed. The available information suggests a low concern for potential risks to children.

Regulatory and Related Information Summary:

- The members of this category are listed on the TSCA Inventory. They are not otherwise regulated under TSCA.
- CASRN 8002-26-4 is listed as an inert substance of unknown toxicity under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).

Assumptions and Uncertainties:

- EPA has no information on releases of these chemicals, and assumes potential exposures based on reported uses.

Rationale Leading To Prioritization Decision:

- Available data suggest a low hazard to the environment and to humans in all potential exposure groups.

Prioritization Decision:

- LOW PRIORITY – Follow-up action not suggested at this time.

Supporting Documentation:

Screening-Level Risk Characterization: September 2008
Screening-Level Hazard Characterization: September 2008
Screening-Level Exposure Characterization: September 2008

Supporting Documents for Initial Risk-Based Prioritization of High Production Volume Chemicals

Rosin and Rosin Salts Category

Rosin (CASRN 8050-09-7)

Rosin, sodium salt (CASRN 61790-51-0)
(9th CI and CA Index Name: Resin acids and Rosin acids, sodium salts)

Rosin, potassium salt (CASRN 61790-50-9)
(9th CI and CA Index Name: Resin acids and Rosin acids, potassium salts)

Rosin, hydrogenated (CASRN 65997-06-0)

Rosin, distillation overheads (CASRN 68425-08-1)
(9th CI and CA Index Name: Rosin, distn. overheads)

Rosin, low-boiling fraction (CASRN 68783-82-4)

Contents:

BACKGROUND

Screening-level hazard, exposure and risk characterizations for high production volume chemicals (HPV) are important contributions to the chemicals cooperation work being done in North America[1] through the EPA Chemical Assessment and Management Program (ChAMP)[2]. These screening-level characterizations are developed by EPA for individual chemicals or chemical categories to support initial Risk-Based Prioritizations (RBPs) for HPV chemicals. These screening-level characterizations are technical documents intended primarily to inform the Agency's internal decision-making process. Accordingly, they are written for assessment professionals and assume a degree of technical understanding. Each of the support documents is described below.

The Risk-Based Prioritizations are found in an accompanying document and are written for a general audience. They present EPA's initial thinking regarding the potential risks presented by these chemicals and future possible actions that may be needed.

Hazard Characterizations for HPV Chemicals

EPA's screening-level hazard characterizations are based primarily on the review of the summaries of studies and other information submitted by the chemical sponsor(s) under the HPV Challenge Program[3]. These studies included in the scope of the HPV Challenge comprise the Screening Information Data Set (SIDS) of the Organization for Economic Cooperation and Development (OECD)[4], an internationally recognized battery of tests that provides the basic data necessary to make an initial evaluation of a chemical's hazards and fate. In preparing the initial hazard characterizations, EPA also consulted a variety of reliable sources[5] for additional relevant information and considered its own comments and public comments on the original submission as well as the sponsor's responses to comments and revisions made to the submission. In order to determine whether any new hazard information was developed since the time of an HPV submission, EPA also searched publicly available databases[6] for information entered from one year prior to the HPV submission through May 2008. The screening-level hazard characterization is performed according to established EPA guidance[7]. A more detailed description of the hazard characterization process is available on the EPA website[8].

With respect to chemicals for which internationally-accepted OECD SIDS Initial Assessment Profiles (SIAP) and Initial Assessment Reports (SIAR) were available, EPA did not generate its own screening-level hazard characterization, but did check for and incorporate updated information in the risk characterization.

Exposure Characterizations for HPV Chemicals

EPA recently received exposure-related data on chemicals submitted in accordance with the requirements of Inventory Update Reporting (IUR).[9] The 2006 IUR submissions pertain to chemicals manufactured in

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[1] U.S. EPA – U.S. Commitments to North American Chemicals Cooperation: http://www.epa.gov/hpv/pubs/general/sppframework.htm.

[2] U.S. EPA – ChAMP information: http://www.epa.gov/champ/.

[3] U.S. EPA – HPV Challenge Program information: http://www.epa.gov/hpv.

[4] U.S. EPA – Technical Guidance Document, OECD SIDS Manual Sections 3.4 and 3.5: http://www.epa.gov/chemrtk/pubs/general/sidsappb.htm.

[5] U.S. EPA – Public Database Hazard Information: http://www.epa.gov/hpvis/hazardinfo.htm.

[6] U.S. EPA – Public Database Update Information: http://www.epa.gov/chemrtk/hpvis/updateinfo.htm.

[7] U.S. EPA – Risk Assessment Guidelines: http://cfpub.epa.gov/ncea/raf/rafguid.cfm.

[8] U.S. EPA – About HPV Chemical Hazard Characterizations: http://www.epa.gov/hpvis/abouthc.htm.

[9] U.S. EPA – Basic IUR Information: http://www.epa.gov/opptintr/iur/pubs/guidance/basic-information.htm.

(including imported into) the U.S. during calendar year 2005 in quantities of 25,000 pounds or more at a single site. The reports include the identity, the quantity, and the physical form of the chemical manufactured or imported, and the number of workers reasonably likely to be exposed during manufacture of the chemical. For chemicals manufactured or imported in quantities of 300,000 pounds or more at a single site, additional reported information includes: the industrial processing and uses of the chemical; the number of industrial processing sites and workers reasonably likely to be exposed to the chemical at those sites; the consumer and commercial uses of the chemical; and an indication whether the chemical was used in products intended for use by children under 14 years of age.

EPA's screening-level exposure characterizations are based largely on the information submitted under the IUR reporting, although other exposure information submitted to the Agency (for example, in HPV submissions) or readily available through a limited set of publicly accessible databases was also considered.[10] was also considered. The screening-level exposure characterizations identify a potential (high, medium, or low) that each of five populations – the environment, the general population, workers, consumers, and children – might be exposed to the chemical. In most cases, this potential doesn't address the quantity, frequency, or duration of exposure, but refers only to the likelihood that an exposure could occur.

In many instances EPA is not able to fully disclose to the public all the IUR exposure-related data reviewed or relied upon in the development of the screening-level documents because some of the material was claimed as confidential business information (CBI) when it was submitted to the Agency. These CBI claims do limit the Agency's ability to be completely transparent in presenting some underlying exposure and use data for chemicals in public documents. EPA does consider all data, including data considered to be CBI, in the screening-level exposure and risk characterization process, and endeavors whenever possible to broadly characterize supporting materials claimed as confidential in ways that do not disclose actual CBI.

Risk Characterizations for HPV Chemicals

EPA combines the information from the screening-level exposure characterization with the screening-level hazard characterization to develop a qualitative screening-level risk characterization, as described in the Agency's guidance on drafting risk characterizations[11]. These screening-level risk characterizations are technical documents intended to support subsequent priority-setting decisions and actions by OPPT. The purpose of the qualitative screening-level risk characterization is two-fold: to support initial risk-based decisions to prioritize chemicals, identify potential concerns, and inform risk management options; and to identify data needs for individual chemicals or chemical categories.

These initial characterization and prioritization documents do not constitute a final Agency determination as to risk, nor do they determine whether sufficient data are available to characterize risk. Recommended actions reflect EPA's relative judgment regarding this chemical or chemical category in comparison with others evaluated under this program, as well as the uncertainties presented by gaps that may exist in the available data.

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[10] U.S. EPA – Summary of Public Databases Routinely Searched: http://www.epa.gov/chemrtk/hpvis/pubdtsum.htm.

[11] U.S. EPA – Risk Characterization Program: http://www.epa.gov/osa/spc/2riskchr.htm

QUALITATIVE SCREENING-LEVEL RISK CHARACTERIZATION OF HIGH PRODUCTION VOLUME CHEMICALS

CHEMICAL CATEGORY NAME
Rosin and Rosin Salts

SPONSORED CHEMICALS

Rosin	CAS No. 8050-09-7
Rosin, sodium salt	CAS No. 61790-51-0
Rosin, potassium salt	CAS No. 61790-50-9
Rosin, hydrogenated	CAS No. 65997-06-0
Rosin, distillation overheads	CAS No. 68425-08-1
Rosin, low boiling fraction	CAS No. 68783-82-4

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QUALITATIVE SCREENING-LEVEL RISK CHARACTERIZATION FOR
Rosin and Rosin Salts Category

1. Category Justification

The six members of the rosin and rosin salts category are all derived from rosin, either by high temperature distillation or by reacting with appropriate bases to form salts. The substances in this category are complex mixtures; also called Class 2 substances, which means they are composed of several chemicals at concentrations that vary depending on their source and methods of derivation. Hydrogenated rosin (CAS No. 65997-06-0) is similar to rosin except that some of the double bonds in the resin acids are saturated. Rosin distillation overheads (CAS No. 68425-08-1) and rosin, low boiling fraction (CAS No. 68783-82-4) are products obtained when rosin is heated to the temperature at which it degrades. The potassium and sodium salts are made by treating rosin with appropriate bases. EPA has concluded that the chemicals in this category can be grouped and evaluated together for the purposes of the HPV Challenge Program as they have similar structure, composition, physical-chemical and environmental fate properties and toxicity to aquatic and mammalian species. EPA further accepts this category for prioritization in the Chemical Assessment and Management Program (ChAMP).

2. Physical-Chemical Properties and Environmental Fate

The members of the rosins and rosin salts category are complex mixtures (Class 2 substances). Many are liquids at room temperature but others are tarry substances or aqueous dispersions. Water solubility is generally low to moderate, except for the rosin salts which are dispersible. Vapor pressures are negligible to low. Most compounds will be minimally mobile in soil and will sorb strongly to solids and sediments in the aquatic environment. Photolysis is of little significance overall, but the small fraction that enters the atmosphere and is not sorbed to aerosols will undergo photooxidation at a rate that is moderate to rapid. Members of this category are expected to biodegrade in the environment slowly; degradability for individual compounds will range from moderate to slow. Hydrolysis is not a significant process and the rate of hydrolysis for the individual compounds for this mixture is negligible. The persistence and bioaccumulation potential of rosin and rosin salts are P2 (moderate) B1 (low) with the exception of rosin, hydrogenated (CAS No. 65997-06-0) which is P3 (high) B1 (low).

3. Hazard Characterization

Aquatic Organism Toxicity. The aquatic toxicity data submitted were generated using the Water Accommodated Fraction method. The evaluation of available toxicity data for fish and aquatic plants indicate the potential hazard to these aquatic organisms is low based on no effects observed at the water solubility limit (saturation) of rosin. The evaluation of available toxicity data for aquatic invertebrates indicates the potential acute hazard to these aquatic organisms is high. The physical-chemical properties and fate characteristics of these chemicals also indicate a potential concern for chronic toxicity.

Human Health Toxicity. Acute oral toxicity for rosins and rosin salts is low. Systemic toxicity in oral repeated-dose studies in rats is low for members of this category. A combined oral reproductive/developmental toxicity study showed low developmental, reproductive and systemic toxicity. The category members were not tested for genetic toxicity. Carcinogenicity studies showed no increase in incidence or type of tumors in rats; however, the reliability of these data is questionable.

4. Exposure Characterization

Five of the six rosin and rosin salts chemicals have aggregated production and/or import volumes in the ranges of 112 million to 570.5 million pounds. The aggregated production volumes exclude that of rosin, low-boiling fraction (CAS# 68783-82-4), which does not have Inventory Update Reporting (IUR) submissions. Non-confidential IUR information for many of the chemicals in the rosin and rosin salts category indicates that these chemicals are used as adhesive and binding agents, intermediates or process regulators in a variety of industries. Four of the six chemicals in this category have IUR submissions that indicate industrial processing and use, as well as commercial or consumer use.

Potential Exposures to the General Population and the Environment: Based on the known uses, which include dispersive commercial and consumer use, releases to all media are likely. Persistence and bioaccumulation ratings for these chemical are P2 and B1, with the exception of rosin, hydrogenated (CAS No. 65997-06-0), which is very persistent, P3, and low bioaccumulation, B1. These ratings suggest that most rosin and rosin salts are moderately persistent in the environment; and are not very bioaccumulative. Based on the information considered, including fate, known uses, and the Agency's expert judgment, EPA identifies a medium potential that the general population and the environment might be exposed.

Potential Exposures to Workers: Based on the information considered, including IUR data and information from public data sources, and in combination with the Agency's professional judgment, EPA identifies a high relative ranking for potential worker exposure. This relative ranking is based on the relatively high number of potentially exposed workers at manufacturing, industrial processing and use sites (100-999 workers for CAS# 65997-03-7 and >1,000 workers for all other chemicals); moderate to high production and/ or import volumes, particularly CAS# 68955-98-6; and a number of industrial processing and uses. These chemicals do not have OSHA Permissible Exposure Limits (PELs).

Potential Exposures to Consumers: EPA has identified, for the purposes of risk-based prioritization, a high potential that consumers might be exposed based on the use of products containing these chemicals. Four of the five chemicals with IUR submissions indicate commercial or consumer uses. There is also potential for exposure to consumers based on information from public data sources. Information from the National Institutes of Health indicates that CAS# 61790-51-0 and CAS# 8050-09-7 are found in household products.

Potential Exposures to Children: EPA has identified, for the purposes of risk-based prioritization, a high potential that children may be exposed based on the use of household products containing these chemicals. One or more companies submitted IUR data that reported uses in products intended to be used by children or, that such information was not readily obtainable or, claimed this information to be confidential.

5. Risk Characterization

The statements and rationale provided below are intended solely for the purpose of this screening-level and qualitative risk characterization and will be used for prioritizing substances for future work in the Chemical Assessment and Management Program (ChAMP).

Risk Statement and Rationale

Potential Risk to Aquatic Organisms from Environmental Releases (LOW/MEDIUM CONCERN). EPA identifies a medium potential that aquatic organisms might be exposed from environmental releases. Although these chemicals display moderate or high persistence, low acute hazard to fish and plants considered in combination with the low bioaccumulation suggest a low concern for potential risk to these aquatic organisms from environmental releases. The high acute hazard to aquatic invertebrates combined with the environmental fate characteristics of most category members of moderate persistence and low bioaccumulation, suggest a medium concern for potential risk to these aquatic organisms.

Potential Risk to the General Population from Environmental Releases (LOW CONCERN). EPA identifies a medium potential that the general population might be exposed from environmental releases. The potential human health hazard is expected to be low due to the lack of specific toxicity to animals following exposure to high doses. Although these chemicals display moderate or high persistence, the low hazard in combination with the low bioaccumulation suggest a low concern for potential risk to the general population from environmental releases.

Potential Risk to Workers (LOW CONCERN). EPA identifies a high relative ranking for potential worker exposure. The potential human health hazard is expected to be low due to the lack of specific toxicity to animals following exposure to high. Therefore, taken together, the available information suggests a low overall concern for potential risks to workers.

Potential Risk to Consumers from Known Uses (LOW CONCERN). EPA identifies a high potential that consumers might be exposed from products containing these chemicals. The potential human health hazard is expected to be low due to the lack of specific toxicity to animals following exposure to high doses. Therefore, taken together, the available information suggests a low concern for potential risks to consumers.

Potential Risk to Children (LOW CONCERN). EPA has identified a high potential that children might be exposed based on the use of products containing these chemicals. The potential human health hazard is expected to be low due to the lack of specific toxicity to young animals following exposure to high doses. Therefore, taken together, the available information suggests a low concern for potential risks to children.

SCREENING-LEVEL HAZARD CHARACTERIZATION OF HIGH PRODUCTION VOLUME CHEMICALS

CHEMICAL CATEGORY NAME

Rosin and Rosin Salts

SPONSORED CHEMICALS

Rosin	CAS No. 8050-09-7
Rosin, sodium salt	CAS No. 61790-51-0
Rosin, potassium salt	CAS No. 61790-50-9
Rosin, hydrogenated	CAS No. 65997-06-0
Rosin, distillation overheads	CAS No. 68425-08-1
Rosin, low boiling fraction	CAS No. 68783-82-4

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SCREENING-LEVEL HAZARD CHARACTERIZATION OF HIGH PRODUCTION VOLUME CHEMICALS

Rosin and Rosin Salts Category

Introduction

The sponsor, Pine Chemicals Association, Inc. submitted a Test Plan and Robust Summaries to EPA for the Rosins and Rosin Salts Category on July 23, 2001. EPA posted the submission on the ChemRTK HPV Challenge website on October 4, 2001 (http://www.epa.gov/chemrtk/pubs/summaries/rosnsalt/c13134tc.htm). EPA comments on the original submission were posted to the website on March 22, 2002. Public comments were also received and posted to the website. The sponsor submitted updated/revised documents on June 3, 2002 and September 7, 2004, which were posted to the ChemRTK website on June 21, 2002 and September 22, 2004, respectively. The Rosin and Rosin Salts Category consists of the following substances:

Rosin	CAS No. 8050-09-7
Rosin, sodium salt	CAS No. 61790-51-0
Rosin, potassium salt	CAS No. 61790-50-9
Rosin, hydrogenated	CAS No. 65997-06-0
Rosin, distillation overheads	CAS No. 68425-08-1
Rosin, low boiling fraction	CAS No. 68783-82-4

This screening-level hazard characterization is based primarily on the review of the Test Plan and Robust Summaries of studies submitted by the sponsor(s) under the HPV Challenge Program. In preparing the hazard characterization, EPA considered its own comments and public comments on the original submission as well as the sponsor's responses to comments and revisions made to the submission. In order to determine whether any new hazard information was developed since the time of the HPV submission, a search of the following databases was made from 2003 to June 2008: the NLM databases (ChemID to locate available data sources including Medline/PubMed, Toxline, HSDB, ATSDR, EPA SRS, etc.), STN/CAS online databases (Registry file for locators, ChemAbs for toxicology data, RTECS, Merck, etc.) and Science Direct. The structures of the sponsored chemicals are included in the appendix. Summary tables of SIDS endpoint data are included in the document. The screening-level hazard characterization for environmental and human health toxicity is based largely on SIDS endpoints and is described according to established EPA or OECD effect level definitions and hazard assessment practices.

Category Justification

The six members of the rosin and rosin salts category are all derived from rosin. The substances in this category are complex mixtures; also called Class 2 substances, which means that they are composed of several chemicals with concentrations that vary depending on their source and methods of derivation. Each category member is derived from rosin, either by high temperature distillation or by reacting with appropriate bases to form salts, and is also a complex mixture. Hydrogenated rosin (CAS No. 65997-06-0) is similar to rosin except that some of the double bonds in the resin acids are saturated. Rosin distillation overheads (CAS No. 68425-08-1) and rosin, low boiling fraction (CAS No. 68783-82-4) are products obtained when rosin is heated to the temperature at which it degrades. The rosin potassium and sodium salts are salts of rosin made by treating rosin with appropriate bases.

Rosin is a naturally occurring substance found predominantly in pine trees and is obtained by chemical or distillation processes from the pulping of pine wood. There are three different types of rosins: gum, wood and tall oil rosin—the type depends on the way it is extracted from the pine tree. Gum rosin is derived by slashing the tree and collecting the gummy exudates, which are further distilled; wood rosin is obtained by solvent extraction of pine wood; and tall oil rosin is obtained by distillation of tall oil (the Tall Oil and Related Substance Category has also been sponsored and assessed under the HPV Challenge Program). Rosin is composed primarily of resin acids, a class of tricyclic carboxylic acids, and contains minor amounts of dimerized rosin and unsaponifiable matter. Chemically, the three rosins are very similar, containing the same resin acids in slightly different ratios, and have the same CAS No. 8050-09-7. The sponsor reported typical compositions of the three types of rosins, as presented in the table below. Representative resin acid structures are depicted in the appendix.

General Composition of Gum, Wood and Tall Oil Rosins			
Components	Gum	Wood	Tall Oil
Abietic acid	20%	45%	35%
Palustric acid	18%	10%	10%
Isopimaric acid	18%	11%	7%
Dehydroabietic acid	4%	8%	20%
Neoabietic acid	18%	7%	4%
Pimaric acid	2%	3%	3%

In comments on the original test plan EPA agreed that rosin, its sodium and potassium salts and hydrogenated rosin are structurally similar and can be evaluated together. However, EPA noted that rosin distillation overheads and rosin low boiling fraction, although similar to each other, are different in composition from the other category members in that they have a lower percentage of rosin acids and higher percentages of fatty acids, hydrocarbons and rosin aldehydes, alcohols and esters. For this reason, EPA recommended additional testing to demonstrate similarity of these substances to rosin. In its revised test plan and data submissions, the sponsor conducted additional testing and demonstrated similar acute toxicity of rosin distillation overheads to the other tested members of the category. Based on these data, EPA has concluded that the chemicals in this category can be grouped and evaluated together as they have similar structure, composition, physical-chemical and environmental fate properties and toxicity to aquatic and mammalian species.

Hazard Characterization

The members of the rosins and rosin salts category are complex mixtures (Class 2 substances). Many are liquids at room temperature but others are tarry substances or aqueous dispersions. Water solubility is generally low to moderate, except for the rosin salts which are dispersible. Vapor pressures are negligible to low. Most compounds will be minimally mobile in soil and will sorb strongly to solids and sediments in the aquatic environment. Photolysis is of little significance overall, but the small fraction that enters the atmosphere and is not sorbed to aerosols will undergo photooxidation at a rate that is moderate to rapid. Members of this category are expected to biodegrade in the environment slowly; degradability for individual compounds will range from moderate to slow. Hydrolysis is not a significant process and the rate of hydrolysis for the individual compounds for this mixture is negligible. The persistence and bioaccumulation potential of rosin and rosin salts are P2 (moderate), B1 (low) with the exception of rosin, hydrogenated (CAS No. 65997-06-0) which is P3 (high), B1 (low).

The aquatic toxicity data submitted were generated using the Water Accommodated Fraction method. The evaluation of available toxicity data for fish and aquatic plants indicate the potential hazard to these aquatic organisms is low based on no effects observed at the water solubility limit (saturation) of rosin. The evaluation of available toxicity data for aquatic invertebrates indicates the potential acute hazard to these aquatic organisms is high. The physical-chemical properties and fate characteristics of these chemicals also indicate a potential concern for chronic toxicity.

Acute oral toxicity for rosins and rosin salts is low. Systemic toxicity in oral repeated-dose studies in rats is low for members of this category. A combined oral reproductive/developmental toxicity study showed low developmental, reproductive and systemic toxicity. The category members were not tested for genetic toxicity. Carcinogenicity studies showed no increase in incidence or type of tumors in rats; however, the reliability of these data is questionable.

Chronic invertebrate toxicity and genetic toxicity testing remain data gaps under the HPV Challenge Program.

1. Physical-Chemical Properties and Environmental Fate

The physical-chemical properties of members of the rosin salt category are summarized in Table 1a, while their environmental fate properties are given in Table 1b. The structures of the compounds are provided in the Appendix.

Physical-Chemical Properties Characterization

Rosin and rosin salts are a complex mixture of chemicals derived from the pulping of pine trees. The rosin potassium and sodium salts (CAS No. 61790-50-9, and CAS No. 61790-51-0, respectively) are the simple alkali metal salts of unmodified rosin and are made by treating rosin with the appropriate base. Rosin, hydrogenated (CAS No. 65997-06-0) has similar composition as rosins; however, the components are all fully saturated acids. Rosin distillation overheads (CAS No. 68425-08-1) and rosin, low boiling fraction (CAS No. 68783-82-4) are produced during the manufacturing process for rosin and consist of rosin acids, hydrocarbons, rosin aldehydes, rosin alcohols, fatty acids, and rosin esters. Many of the category members are liquids at room temperature but others are tarry substances or aqueous dispersions. Water solubility is generally low to moderate, except for the rosin salts which are dispersible. Vapor pressures are negligible to low.

Table 1a. Physical-Chemical Properties of Rosins and Rosin Salts[1]

	Rosin	**Rosin, sodium salt**	**Rosin, potassium salt**	**Rosin, hydrogenated**	**Rosin, low boiling fraction**	**Rosin, distillation overheads**
CAS No.	8050-09-7	61790-51-0	61790-50-9	65997-06-0	68783-82-4	68425-08-1
Melting point[2]	No data	No data	No data	No data	No data	No data
Boiling point[2]	No data	No data	No data	No data	No data	No data
Vapor pressure[2]	No data	No data	No data	No data	No data	No data
Log K_{ow}	**1.9 – 7.7 (m)**	**3.5 – 6.6 (m)**	**3.0 – 7.0 (m)**	**2.5 – 7.6 (m)**	**2.5 – 7.8 (m)**	**2.5 – 7.8 (m)**
Water solubility	**0.95 mg/L at 20°C (m)**	**Dispersible (m)**	**Dispersible (m)**	**1.18 mg/L at 20°C (m)**	**19.85 mg/L at 20°C (m)**	**19.85 mg/L at 20°C(m)**

(m) = measured data

[1] Pine Chemicals Association. 2004. Robust Summaries for Rosins and Rosin Salts, http://www.epa.gov/chemrtk/pubs/summaries/rosnsalt/c13134tc.htm

[2] No measured data are available for the individual constituents of the mixture. These complex mixtures will not have a well defined melting or boiling point and the vapor pressure and Henry's Law constant are extremely low since the individual fatty acids exist as anions at environmental pH.

Environmental Fate Characterization

The constituents of rosin and rosin salts will be minimally mobile in the environment and will adsorb strongly to sediments or suspended solids in water bodies. Based on the results of biodegradation screening studies for these complex mixtures, the components of rosin and rosin salts are expected to biodegrade at rates that are moderate to slow. Rosin and rosin salts will be minimally volatile from moist soil and water surfaces since most of the constituents are ionic. Hydrolysis is expected to be negligible since the components of these mixtures do not possess hydrolyzable functional groups. The potential for bioconcentration in aquatic organisms for the components of these mixtures is expected to be low. The persistence and bioaccumulation potential of rosin and rosin salts are moderate (P2) and low (B1), respectively; with the exception of rosin, hydrogenated which is high (P3) and low (B1), respectively.

Table 1b. Environmental Fate Properties of Rosins and Rosin Salts[1]

	Rosin	**Rosin, sodium salt**	**Rosin, potassium salt**	**Rosin, hydrogenated**	**Rosin, low boiling fraction**	**Rosin, distillation overheads**
CAS No.	8050-09-7	61790-51-0	61790-50-9	65997-06-0	68783-82-4	68425-08-1
Photodegradation half-life[2]	0.5 – 5 hours	0.5 – 5 hours	0.5 – 5 hours	4 – 5 hours	0.5 – 5 hours	0.5 – 5 hours
Biodegradation	**32% (m)** after 28 days (not readily biodegradable)	32% after 28 days (not readily biodegradable) (RA)	32% after 28 days (not readily biodegradable) (RA)	**0.95% (m)** after 28 days (not readily biodegradable)	30% after 28 days (not readily biodegradable) (RA)	**30% (m)** after 29 days (not readily biodegradable)
Hydrolysis	Stable	Stable	Stable	Stable	Stable	Stable
K_{oc}[2]	21,990 – 40,550	21,990 – 40,550	21,990 – 40,550	21,990 – 40,550	21,990 – 40,550	21,990 – 40,550
BCF[2]	10 – 56	10 – 56	10 – 56	10 – 56	10 – 56	10 – 56
Persistence[3]	P2 (moderate)	P2 (moderate)	P2 (moderate)	P3 (high)	P2 (moderate)	P2 (moderate)
Bioaccumulation[3]	B1 (low)	B1 (low)	B1 (low)	B1 (low)	B1 (low)	B1 (low)

(m) = measured data; (RA) = Read-Across

[1] Pine Chemicals Association. 2004. Robust Summaries for Rosins and Rosin Salts, http://www.epa.gov/chemrtk/pubs/summaries/rosnsalt/c13134tc.htm

[2] USEPA. 2007. EPI v3.12 PC-Computer software developed by EPA's Office of Pollution Prevention Toxics and Syracuse Research Corporation. http://www.epa.gov/opptintr/exposure/pubs/episuite.htm.

[3] FR. 1999. Category for Persistent, Bioaccumulative, and Toxic New Chemical Substances. *Federal Register* 64, Number 213 (November 4, 1999) Page 60194-60204.

Summary - Conclusions

The members of the rosins and rosin salts category are complex mixtures (Class 2 substances). Many are liquids at room temperature but others are tarry substances or aqueous dispersions. Water solubility is generally low to moderate, except for the rosin salts which are dispersible. Vapor pressures are negligible to low. Most compounds will be minimally mobile in soil and will sorb strongly to solids and sediments in the aquatic environment. Photolysis is of little significance overall, but the small fraction that enters the atmosphere and is not sorbed to aerosols will undergo photooxidation at a rate that is moderate to rapid. Members of this category are expected to biodegrade in the environment slowly; degradability for individual compounds will range from moderate to slow. Hydrolysis is not a significant process and the rate of hydrolysis for the individual compounds for this mixture is negligible. The persistence and bioaccumulation potential of rosin and rosin salts are P2 (moderate), B1 (low) with the exception of rosin, hydrogenated (CAS No. 65997-06-0) which is P3 (high), B1 (low).

2. Environmental Effects – Aquatic Toxicity

A summary of aquatic toxicity data submitted for SIDS endpoints is provided in Table 2. The table also indicates where data for tested category members are read-across (RA) to untested members of the category.

Acute Toxicity to Fish

Rosin (CAS No. 8050-09-7)

Fathead minnows (*Pimephales promelas*) were exposed to the test substance as water accommodated fractions (WAFs) under static conditions for 96 hours. The loading rates were 0, 1, 10, 100 or 1000 mg/L and no analytical measurements were made on the WAFs. No effects were noted at any of the WAF loading rates. EPA does not consider the loading rate as the no effect concentration when the concentration exceeds the water solubility of the

substance. Assuming exposure concentration in the WAF is the water solubility limit (saturation) for rosin, the no effect concentration would be approximately 0.9 mg/L.
No effects at saturation

Acute Toxicity to Aquatic Invertebrates

Rosin (CAS No. 8050-09-7)
Daphnia magna were exposed to the test substance as water accommodated fractions (WAFs) under static conditions for 48 hours. The loading rates were 0, 125, 250, 500 and 1000 mg/L and no analytical measurements were made on the WAFs. Exposure to the 1000 mg/L WAF resulted in 50% mortality at 24 hours and 85% mortality at 48 hours. The sponsor reported the 48-h EL$_{50}$ as 911 mg/L and no effect loading rate as 750 mg/L. EPA does not consider the loading rate as the effect concentration when the concentration exceeds the water solubility of the substance. Assuming exposure concentration in the WAF is the water solubility limit (saturation) for rosin, the 24-h LC$_{50}$ would be approximately 0.9 mg/L and the 48-h LC$_{50}$ would be less than 0.9 mg/L, both indicative of high acute toxicity to aquatic invertebrates.

Toxicity to Aquatic Plants

Rosin (CAS No. 8050-09-7)
Green algae *(Pseudokirchneriella subcapitata)* were exposed to the test substance as water accommodated fractions (WAFs) under static conditions for 72 hours. The loading rates were 0, 1, 10, 100 or 1000 mg/L and no analytical measurements were made on the WAFs. No effects were noted at any of the WAF loading rates. EPA does not consider the loading rate as the no effect concentration when the concentration exceeds the water solubility of the substance. Assuming exposure concentration in the WAF is the water solubility limit (saturation) for rosin, the no effect concentration would be approximately 0.9 mg/L.
No effects at saturation

Conclusion: The aquatic toxicity data submitted were generated using the Water Accommodated Fraction method. The evaluation of available toxicity data for fish and aquatic plants indicate the potential hazard to these aquatic organisms is low based on no effects observed at the water solubility limit (saturation) of rosin. The evaluation of available toxicity data for aquatic invertebrates indicates the potential hazard to these aquatic organisms is high.

In comments on the original test plan, EPA recommended that the sponsor conduct chronic toxicity testing on invertebrates (i.e., the daphnid 21-day reproduction test). While the acute testing did not show toxicity in fish and aquatic plants, the physical-chemical properties of the substances in this category indicate they are soluble or miscible in water at concentrations that could cause chronic effects. Furthermore, the acute testing of aquatic invertebrates demonstrated high acute toxicity for these organisms. Therefore, the chronic invertebrate toxicity test remains a data gap under the HPV Challenge Program.

Table 2. Summary of Environmental Effects – Aquatic Toxicity Data

Endpoints	**Rosin (8050-09-7)**	**Rosin, sodium salt (61790-51-0)**	**Rosin, potassium salt (61790-50-9)**	**Rosin, hydrogenated (65997-06-0)**	**Rosin, low boiling fraction (68783-82-4)**	**Rosin, distillation overheads (68425-08-1)**
Fish 96-h LC$_{50}$ (mg/L)	**NES[1]**	No Data NES[1] (RA)	No Data NES[1] (RA)	No Data NES[1] (RA)	No Data NES[1] (RA)	No Data NES[1] (RA)
Aquatic Invertebrates 48-h EC$_{50}$ (mg/L)	**< 0.9**	No Data < 0.9 (RA)	No Data < 0.9 (RA)	No Data < 0.9 (RA)	No Data < 0.9 (RA)	No Data < 0.9 (RA)
Aquatic Plants 72-h EC$_{50}$ (mg/L)	**NES[1]**	No Data NES[1] (RA)	No Data NES[1] (RA)	No Data NES[1] (RA)	No Data NES[1] (RA)	No Data NES[1] (RA)

[1] NES = No effects at saturation (water solubility limit); (RA) = Read Across

3. Human Health Effects

A summary of health effects data submitted for SIDS endpoints is provided in Table 3. The table also indicates where data for tested category members are read-across (RA) to untested members of the category.

Acute Oral Toxicity

Rosin (CAS No. 8050-09-7)
Multiple acute oral toxicity data for three different forms of rosin – gum, wood and tall oil – were submitted.

Gum Rosin
Rats, mice and guinea pigs received unspecified graded doses of gum rosin in corn oil via oral gavage and were observed for 14 days.
LD_{50} (rat) = 7600 mg/kg-bw
LD_{50} (mouse) = 4600 mg/kg-bw
LD_{50} (guinea pig) = 4100 mg/kg-bw

Wood Rosin
Rats, mice and guinea pigs received unspecified graded doses of wood rosin in corn oil via oral gavage and were observed for 14 days.
LD_{50} (rat) = 8400 mg/kg-bw
LD_{50} (mouse) = 4100 mg/kg-bw
LD_{50} (guinea pig) = 4100 mg/kg-bw

Tall Oil Rosin
Rats, mice and guinea pigs received unspecified graded doses of tall oil rosin in corn oil via oral gavage and were observed for 14 days.
LD_{50} (rat) = 7600 mg/kg-bw
LD_{50} (mouse) = 4600 mg/kg-bw
LD_{50} (guinea pig) = 4600 mg/kg-bw

Rosin, hydrogenated (CAS No. 65997-06-0)
Wistar Rats (10/sex) were administered hydrogenated rosin as a single oral dose of 30 mL/kg-bw (approximately 31,500 mg/kg-bw base on density of 1.05 g/mL) and were observed for 14 days. No deaths occurred.
LD_{50} > 31,500 mg/kg-bw

Rosin, distillation overheads (CAS No. 68425-08-1)
Female Sprague-Dawley rats (5) were administered rosin, distillation overheads as a single dose in corn oil via gavage and were observed for 14 days. All rats survived.
LD_{50} > 2000 mg/kg-bw

Repeated-Dose Toxicity

Five of the submitted repeated-dose toxicity studies were conducted at the Industrial Bio-Test Laboratories (IBT), Inc. Based on guidance on the acceptance and use of IBT studies (as discussed in the Organization for Economic Cooperation and Development's SIDS Initial Assessment Meeting 21), when the study has not been audited by either EPA or FDA or by Industry, and if the findings of the IBT study were consistent with a study conducted at later date in another laboratory, then the data may be used but should be considered as weak evidence. As summarized below, toxicity data derived from the reproductive/developmental toxicity study are consistent with the IBT data.

Rosin (CAS No. 8050-09-7)
(1) Five separate dietary studies in rats (one using gum rosin, two using wood rosin and two using rosin with no trade name given) were conducted by IBT Laboratories in 1960. Each was a 90-day repeated-dose toxicity study where Sprague-Dawley rats (10/sex/treatment) were exposed to rosin in the diet at concentrations of 0, 0.01, 0.05, 0.2, 1.0 or 5.0% (approximately corresponding to 0, 10, 50, 200, 1000 or 5000 mg/kg-bw/day). In all 5 studies,

animals exposed to 5% rosin exhibited weight loss and a marked decrease in food consumption followed by mortality. Starvation through refusal to eat (possibly related to palatability) was stated as the primary cause of death. At 1% dietary exposure, reduced food consumption, decreased mean body weight and decreased body weight gain were reported. No treatment-related effects on hematology or urinalysis parameters were reported in any study. At necropsy, no treatment-related changes were noted. An increase in absolute liver weights was reported in three of the five studies and relative organ weights were reported as 'altered' in two studies and increases in relative organ weights (liver, kidney and/ or spleen) were reported in three studies. Histological changes in kidneys of high dose animals were found in one study. No histopathological findings were indicated in the remaining four studies. No evidence of toxicity to reproductive organs was observed at any dose level in any of the five studies.
LOAEL ~ 1000 mg/kg-bw/day (based on reduced body weight and increased absolute and relative organ weights)
NOAEL ~ 200 mg/kg-bw/day

(2) The systemic toxicity data derived from the reproductive/developmental toxicity study (conducted at Inveresk Research in 2002) on rosin is consistent with results of the IBT studies. Sprague-Dawley rats (10/sex/dose) were administered rosin via the diet at concentrations of 0, 1000, 3000 and 10,000 ppm (approximately corresponding to 0, 105, 275 or 825 mg/kg-bw/day). The males were dosed for at least 4 weeks, starting from 2 weeks prior to mating. The females were dosed from 2 weeks prior to mating until at least day 4 of lactation. Treatment with rosin at 10,000 ppm was associated with reduced weight gain and weight loss and reduced food consumption for the first few weeks of treatment. Food consumption was reduced throughout gestation and body weight gain was reduced during the first half of gestation. Body weight gain was slightly reduced in males at 3000 ppm (275 mg/kg-bw/day). However, none of the observed effects are reported as significantly different from controls in the robust summary. Observable effects (changes that are not clearly adverse or statistically significant) are reported at 275 mg/kg-bw/day.
NOAEL (systemic toxicity) ~ 825 mg/kg-bw/day (no effects at highest dose tested)

Rosin, hydrogenated (CAS No. 65997-06-0)
In an unaudited study by IBT Laboratories, Sprague-Dawley rats (10/sex/group) were administered hydrogenated rosin in the diet at concentrations of 0, 0.01, 0.05, 0.2, 1 or 5% (approximately corresponding to 0, 10, 50, 200, 1000 or 5000 mg/kg-bw/day) for 90 days. All of the animals in the high-dose group died prior to study termination. These deaths occurred between study day 3 and 11 and were attributed to starvation through food refusal (i.e., treatment-related, marked decrease in food consumption). Rats in this group expressed weight loss. In the 1% dose group, food consumption and body weight were decreased in both males and females. With the exception of the first week of dosing, food utilization (grams gained/gram food consumed) was not affected at a dietary concentration of 1% indicating that the reduced food consumption may have been related to palatability. No treatment-related effects on hematology, urinalysis or gross or microscopic pathology were observed. Organ weight effects were also reported in the 1% dose group. Reproductive organs (i.e., testes, ovaries and uterus) showed no evidence of toxicity at any dose level.
LOAEL ~ 1000 mg/kg-bw/day (based on reduced body weight and organ weight effects)
NOAEL ~ 200 mg/kg-bw/day

Reproductive/Developmental Toxicity

Rosin (CAS No. 8050-90-7) Sprague-Dawley rats (10/sex/dose) were administered rosin via the diet at concentrations of 0, 1000, 3000 and 10,000 ppm (approximately corresponding to 0, 105, 275 or 825 mg/kg-bw/day). The males were dosed for at least 4 weeks, starting from 2 weeks prior to mating. The females were dosed from 2 weeks prior to mating until at least day 4 of lactation. Treatment with rosin at 10,000 ppm was associated with reduced weight gain and weight loss and reduced food consumption for the first few weeks of treatment. Food consumption was reduced throughout gestation and body weight gain was reduced during the first half of gestation. At 10,000 ppm (825 mg/kg-bw/day), the mean number of implantation sites per pregnancy was slightly decreased resulting in a subsequent reduction in litter size. Mean litter and pup weights were also slightly reduced. The effects on implantation, litter size and fetal weight were likely secondary to the effects on food intake and subsequent reduced weight gain in the adult females. Litter survival, as indicated by the birth index and viability index, was similar in all groups. There were no effects of treatment on mating performance, fertility or duration of gestation. No obvious external abnormalities were noted in the pups at any dose level. Testes and epididymides weights were similar in all groups. No histological findings could be attributed to treatment with rosin. Body

weight gain was slightly reduced in males at 3000 ppm (275 mg/kg-bw/day). However, none of the observed effects are reported as significantly different from controls in the robust summary.
NOAEL (maternal toxicity) ~ 825 mg/kg-bw/day (no effects at highest dose tested)
NOAEL (developmental toxicity) ~ 825 mg/kg-bw/day (no effects at highest dose tested)

Genetic Toxicity

No data were submitted for gene mutation and chromosomal aberration endpoints. Instead, PCA submitted negative cancer bioassays as a suitable surrogate for genetic toxicity testing. However, the negative carcinogenicity studies were conducted at IBT and there is no evidence that data from these studies were audited by EPA or FDA. Therefore, their adequacy is questionable. Therefore, the genetic toxicity endpoints are data gap under the HPV Challenge Program.

Additional Information

Carcinogenicity
The carcinogenicity studies submitted were conducted at the Industrial Bio-Test Laboratories (IBT), Inc. Based on guidance on the acceptance and use of IBT studies (as discussed in the Organization for Economic Cooperation and Development's SIDS Initial Assessment Meeting 21), when the study has not been audited by either EPA or FDA or by Industry, and if the findings of the IBT study were consistent with a study conducted at later date in another laboratory, then the data may be used but should be considered as weak evidence. There is no evidence that data from these studies were audited by EPA or FDA. In addition, there is no study of comparable length by an independent laboratory. Therefore, their reliability is questionable.

Gum rosin (CAS No. 8050-09-7)
Sprague-Dawley rats (30/sex/dose) were exposed to gum rosin at dietary concentrations of 0, 0.05 or 1% (approximately 0, 50 or 1000 mg/kg-bw/day) for 2 years. No treatment-related increase in mortality was reported and the only clinical signs were generalized inactivity and weakness in the animals dying on study. Mean body weight and body weight gain were markedly decreased at 1% treatment. Food consumption was also decreased in the high-dose group, but food utilization was unaffected. The effects on body weight and food consumption were attributed to the palatability of the test diet. No treatment-related effects were reported on hematology, urinalysis, and gross and microscopic pathology parameters. Relative liver weights were increased at 1% treatment. Reproductive organs (i.e., testes, ovaries and uterus) showed no evidence of toxicity at any dose level. The tumor incidence and tumor types were similar in the test and control groups. Dietary administration of rosin up to approximately 1% in the diet (approximately 1000 mg/kg-bw/day) did not show increase in the incidence of tumor in rats. The reliability of this unaudited IBT study is questionable.

Rosin, hydrogenated (CAS No. 65997-06-0)
Sprague-Dawley rats (30/sex/dose) were exposed to hydrogenated rosin at dietary concentrations of 0, 0.05, 0.2 or 1% (approximately equivalent to 0, 50, 200 or 1000 mg/kg-bw/day) for 2 years. No treatment-related increase in mortality occurred and the only clinical signs were lethargy in animals near death on study. A decrease in body weight gain was noted in the 1% dose group at the interim sacrifice (12 months) only. Body weights were also decreased in this group at the 12-month time point. After 24 months, no effect of treatment on body weight or body weight gain was observed. Food consumption was decreased in the high-dose group. No effects on hematology, urinalysis, organ weights and gross and microscopic pathology were reported. Reproductive organs (i.e., testes, ovaries and uterus) showed no evidence of toxicity at any dose level. The tumor incidence and tumor types were similar in the test and control groups. Dietary administration of rosin up to 1% in the diet (approximately 1000 mg/kg-bw/day) did not show increase in the incidence of tumor in rats. The reliability of this unaudited IBT study is questionable.

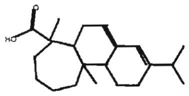
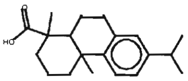
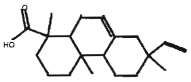
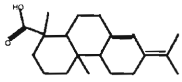
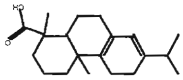
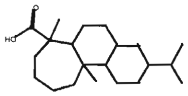
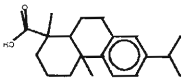
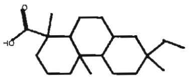
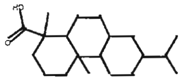
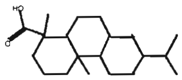
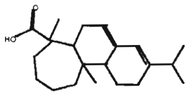
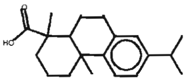
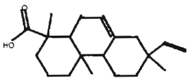
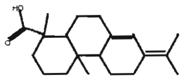
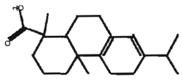
Conclusion: Acute oral toxicity for rosins and rosin salts is low. Systemic toxicity in oral repeated-dose studies in rats is low for members of this category. A combined oral reproductive/developmental toxicity study showed low developmental, reproductive and systemic toxicity. The category members were not tested for genetic toxicity. Carcinogenicity studies showed no increase in incidence or type of tumors in rats; however, the reliability of these data is questionable.

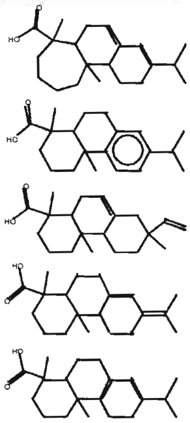
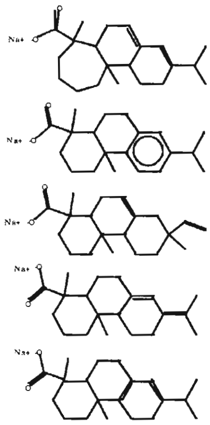
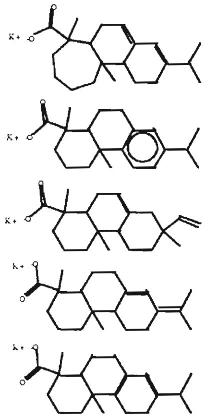
Table 3. Summary of Human Health Data

Endpoints	**Rosin** **(8050-09-7)**	**Rosin, sodium salt** **(61790-51-0)**	**Rosin, potassium salt** **(61790-50-9)**	**Rosin, hydrogenated** **(65997-06-0)**	**Rosin, low boiling fraction** **(68783-82-4)**	**Rosin, distillation overheads** **(68425-08-1)**
Acute Oral Toxicity LD$_{50}$ (mg/kg-bw)	**4100 – 8400**	No Data 4100 – 8400 (RA)	No Data 4100 – 8400 (RA)	**> 31,500**	No Data > 2000 (RA)	**> 2000**
Repeated-Dose Toxicity NOAEL/ LOAEL (mg/kg-bw/day)	**NOAEL ~ 200** **LOAEL ~ 1000**	No Data NOAEL ~ 200 LOAEL ~ 1000 (RA)	No Data NOAEL ~ 200 LOAEL ~ 1000 (RA)	**NOAEL ~ 200** **LOAEL ~ 1000**	No Data NOAEL ~ 200 LOAEL ~ 1000 (RA)	No Data NOAEL ~ 200 LOAEL ~ 1000 (RA)
Reproductive/ Developmental Toxicity (mg/kg-bw/day)						
Systemic Toxicity	**NOAEL ~ 825**	No Data NOAEL ~ 825	No Data NOAEL ~ 825	No Data NOAEL ~ 825	No Data NOAEL ~ 825	No Data NOAEL ~ 825
Reproductive/ Developmental Toxicity	**NOAEL ~ 825**	NOAEL ~ 825 (RA)	NOAEL ~ 825 (RA)	NOAEL ~ 825 (RA)	NOAEL ~ 825 (RA)	NOAEL ~ 825 (RA)
Genetic Toxicity – Gene Mutation	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap
Genetic Toxicity – Chromosomal Aberrations	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap
Other – Carcinogenicity	Data available[1]	Not part of SIDS	Not part of SIDS	Data available[1]	Not part of SIDS	Not part of SIDS

Measured data in bold text; (RA) = Read Across; — indicates that endpoint was not addressed for this chemical[1]. The carcinogenicity studies submitted were conducted at the Industrial Bio-Test Laboratories (IBT), Inc. Based on guidance on the acceptance and use of IBT studies (as discussed in the Organization for Economic Cooperation and Development's SIDS Initial Assessment Meeting 21), when the study has not been audited by either EPA or FDA or by Industry, and if the findings of the IBT study were consistent with a study conducted at later date in another laboratory, then the data may be used but should be considered as weak evidence. There is no evidence that data from these studies were audited by EPA or FDA. Therefore, their reliability is questionable.

Appendix

Rosins and Rosin Salts		
CAS Reg. No.	**Chemical Name**	**Representative structures [1]**
SPONSORED CHEMICALS		
8050-09-7	Rosin[2]	    
65997-06-0	Rosin, hydrogenated[5]	    
68425-08-1	Rosin, distillation overheads[6]	    

Rosins and Rosin Salts		
CAS Reg. No.	**Chemical Name**	**Representative structures [1]**
SPONSORED CHEMICALS		
68783-82-4	Rosin, low boiling fraction[6]	
61790-51-0	Rosin, sodium salt[3]	
61790-50-9	Rosin, potassium salt[4]	

Rosins and Rosin Salts		
CAS Reg. No.	Chemical Name	Representative structures [1]
SPONSORED CHEMICALS		

[1] Principle constituents are typical for each member of this class.

[2] The principle constituents of rosins (tall oil, gum, wood) are approximately: abietic acid (20-45%); dehydroabietic acid (4-20%); isopimaric acid (7-18); neoabietic acid (4-18%); and palustric acid (10-18%). Other constituents include pimiric acid, communic acid, high boiling fatty acids, and unsaponifiable matter.

[3] Produced from rosin treated with sodium hydro xide. The composition is complex but probably consists largely of the sodium salts of the rosin acids.

[4] Produced from rosin treated with potassium hydroxide. The composition is complex but probably consists largely of the potassium salts of the rosin acids.

[5] The principle constituents are similar to rosins, but the conjugated double bonds are prone to oxidation.

[6] The chemical composition is a complex mixture of rosin acids, hydrocarbons, rosin aldehydes, rosin alcohols, fatty acids, and rosin esters.

Screening Level Exposure Characterization for HPV Challenge Chemical

Rosin and Rosin Salts Category

Rosin	CAS No. 8050-09-7
Rosin, sodium salt	CAS No. 61790-51-0
Rosin, potassium salt	CAS No. 61790-50-9
Rosin, hydrogenated	CAS No. 65997-06-0
Rosin, distillation overheads	CAS No. 68425-08-1
Rosin, low boiling fraction	CAS No. 68783-82-4

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Screening Level Exposure Characterization

Rosin and Rosin Salts Category

Non-CBI Executive Summary

The six rosin and rosin salts chemicals have aggregated production and/or import volumes in the ranges of 112 million to 570.5 million pounds[12]. These aggregated volumes exclude that of Rosin, low-boiling fraction (CAS# 68783-82-4), which does not have Inventory Update Reporting (IUR) submissions. Non-confidential IUR information for many of the chemicals in the rosin and rosin salts category indicates that these chemicals are used as adhesive and binding agents, intermediates or process regulators in a variety of industries. Four of the six chemicals in this category have IUR submissions that indicate industrial processing and use, as well as commercial or consumer use.

Potential Exposures to the General Population and the Environment: Based on the known uses, which include dispersive commercial and consumer use, releases to all media are likely. A search of additional relevant databases did not provide further information on releases of these chemicals.

Persistence and bioaccumulation ratings for these chemical are P2 and B1, with the exception of rosin, hydrogenated (CAS No. 65997-06-0), which is very persistent, P3, and low bioaccumulation, B1[13]. These ratings suggest that most rosin and rosin salts are moderately persistent in the environment; and are not very bioaccumulative. Members of this category are expected to biodegrade in the environment slowly. Most compounds will be minimally mobile in soil and will adsorb strongly to solids and sediments in the aquatic environment. Vapor pressures are negligible to low. Based on the information considered, including fate, known uses, and the Agency's expert judgment, EPA identifies a medium potential that the general population and the environment might be exposed.

Potential Exposures to Workers: Based on the information considered, including IUR data and information from public data sources, and in combination with Agency's professional judgment, EPA identifies a high relative ranking for potential worker exposure. This relative ranking is based on the relatively high number of potentially exposed workers at manufacturing, industrial processing and use sites (100-999 workers for CAS# 65997-03-7 and >1,000 workers for all other chemicals); moderate to high production and/ or import volumes, particularly CAS# 68955-98-6; and a number of industrial processing and uses. These chemicals do not have OSHA Permissible Exposure Limits (PELs)[14].

Potential Exposures to Consumers: EPA has identified, for the purposes of risk-based prioritization, a high potential that consumers might be exposed based on the use of products containing these chemicals. Four of the six chemicals have IUR submissions that indicate commercial or consumer uses. One of the six chemicals does not have any IUR submissions.

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[12] USEPA, 2006. Partial Updating of TSCA Chemical Inventory.

[13] USEPA, 2008. Hazard Characterization of Rosin and Rosin Salts Category (CAS No. 65997-06-0).

[14] NIOSH, 1988. OSHA PEL Project Documentation. http://www.cdc.gov/niosh/pel88/npelcas.html. Accessed, 7/11/08.

There is also potential for exposure to consumers based on information from public data sources. Information from the National Institutes of Health indicates that CAS# 61790-51-0 and CAS# 8050-09-7 are found in household products[15].

Potential Exposures to Children: EPA has identified, for the purposes of risk-based prioritization, a high potential that children may be exposed based on the use of household products containing these chemicals. One or more companies submitted IUR data that reported uses in products intended to be used by children or, that such information was not readily obtainable or, claimed this information to be confidential.

Volume and Use Information

Five of the six rosin and rosin salts chemicals have aggregated production and/or import volumes in the ranges of 112 million to 570.5 million pounds[16]. These aggregated volumes exclude that of Rosin, low-boiling fraction (CAS# 68783-82-4), which does not have IUR submissions. Non-confidential information in the IUR indicates that these chemicals were manufactured and/or imported at the following companies:

CAS# 8050-09-7:

- Aceto Corporation
- Akzo Nobel Coatings Inc.
- Ashland Inc.
- Bayer Material Science
- Eastman Chemical Company
- FRP Services & Co. (America) Inc.
- Gehring-Montgomery, Inc.
- Georgia-Pacific Corporation
- Hercules Incorporated
- Palmer Holland Inc.
- Sojitz Corporation of America
- TR International, Incorporated

CAS# 61790-51-0:

- Akzo Nobel Coatings Inc.
- Asphalt Materials, Inc.
- DuPont Performance Elastomers LLC
- Flint Hills Resources, LP
- Hercules Incorporated
- Heritage Synfuel Binders, LLC

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[15] National Institutes of Health, 2008. Household Product Database. Accessed, 7/11/08. http://hpd.nlm.nih.gov/products.htm

[16] USEPA, 2006 Partial Updating of TSCA Chemical Inventory.

CAS# 61790-50-9:

- Akzo Nobel Coatings Inc.
- DuPont Performance Elastomers LLC
- Eastman Chemical Company
- Georgia-Pacific Corporation
- Hercules Incorporated
- W.R. Grace, Performance Chemicals

CAS# 65997-06-0:

- Ciba Specialty Chemicals Corp.
- Eastman Chemical Company
- Flint Group North America Corporation
- H.B. Fuller Company
- Hercules Incorporated

CAS# 68425-08-1:

- Hercules Incorporated

There may be other companies that are claimed confidential. Persons submitting IUR information for 2005 asserted that some or all of the information was confidential. Only non-confidential information reported in IUR is included in this exposure characterization.

The IUR submissions include a variety of industrial processing and uses. The non-confidential industrial processing uses are listed in Table 1 at the end of this summary. The IUR submissions also include several commercial and consumer uses. These uses are listed in Table 2 at the end of this summary.

The High Production Volume (HPV) Challenge Program submission for the rosins and rosin → salts category chemicals states that rosin (CAS# 8050-09-7) is mainly used in the production of derivatives or chemical intermediates that have various industrial applications, particularly in the production of printing inks, adhesives, chewing gum and coatings[17]. The sodium salts of rosin (CAS# 61790-51-0) are used in paper sizing chemicals to give the finished product a better surface finish and water resistance. Potassium salts of rosin (CAS# 61790-50-9) are used in the production of various soaps and detergents. Rosin, hydrogenated (CAS# 65997-06-0) is used in specialty adhesive applications where product stability and color are important. Rosin, distillation overheads (CAS# 68425-08-1) and rosin, low boiling fraction (CAS# 68783-82-4) are used in the production of rosin derivatives for the end use applications described above, or if the quality of the substances is undesirable, they may be consumed for their fuel value.

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[17] Pine Chemicals Association, 2004. High Production Volume Final Submission for Rosins and Rosin Salts. September 2004. Accessed 7/11/08 at http://www.epa.gov/HPV/pubs/summaries/rosnsalt/c13134ft.pdf.

Exposures to Workers

Based on the information considered, including IUR data and information from public data sources, and in combination with Agency's professional judgment, EPA has identified for the purposes of risk-based prioritization, a high relative ranking for potential worker exposure. This relative ranking is based on the relatively high number of potentially exposed workers at manufacturing, industrial processing and use sites; moderate to high production and/ or import volumes, particularly CAS# 68955-98-6; and a number of industrial processing and uses.

Summary of Parameters Affecting Worker Exposure

Parameter	
Volume *	112 million to 570.5 million pounds
Physical Form(s) *	Liquid; solid; pellets or large crystals; dry powder
Vapor Pressure	Negligible to low
Concentration*	Greater than 90% by weight
Number of Industrial Workers *	1,000 or greater
Uses*	adhesive and binding agents, intermediates or process regulators
Key MSDS Info (MSDS found for CAS#65997-06-0 and CAS#8050-09-7 only)	wear NIOSH-approved respirator, safety glasses and rubber gloves[18]
Other hazard characteristics	may cause eye, skin, respiratory and digestive tract irritation

* Only non-confidential IUR data are included in this summary.

Based on IUR data, the maximum total number of workers reasonably likely to be exposed to this chemical during manufacturing and industrial processing and use may be 1,000 or greater (between 100 to 999 workers for CAS# 65997-03-7, and 1,000 or greater for all other chemicals in this category). There may be additional potentially exposed industrial workers that are not included in this estimate since not all submitters were required to report industrial processing and use and/or there is at least one use that contains a "Not Readily Obtainable" (NRO) response among the submissions. This estimate does not include the number of potentially exposed commercial workers which is generally assumed to be high. The National Occupational Exposure Survey (NOES), conducted from 1981 to 1983, estimated a total of 39,413 workers potentially exposed to CAS# 61790-50-9; 32,938 workers potentially exposed to CAS# 61790-51-0; and 93,886 workers potentially exposed to CAS# 65997-06-0[19]. Differences between number of workers estimated by IUR submitters and by the NOES are attributable to many factors, including time, scope, and method of the estimates. For example,

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[18] PDM Inc, 2003. MSDS: CAS# 65997-06-0. www.pdmchemicals.com/MSDS/MSDS-Resin%20H.doc. Acros Organics, 2001. MSDS: CAS# 8050-09-7. www.acros.com. Accessed, 7/18/08.

[19] NIOSH, 1983. National Occupational Exposure Survey (NOES, 1981-1983). Accessed, 7/11/08. http://www.cdc.gov/noes.

NOES estimates are for all workplaces while IUR are for industrial workplaces only, and NOES used a survey and extrapolation method while IUR submitters simply provide their best estimates based on available information for the specific reporting year.

Based on IUR data, these chemicals are manufactured in various physical forms, including liquid, solid, dry powder, pellets or large crystals, and worker exposures are possible for chemicals in these forms. There may be other physical forms that are claimed confidential. Also, the non-confidential maximum concentration is up to 100% by weight.

These chemicals do not have OSHA Permissible Exposure Limits (PELs)[20].

Environmental Releases

Environmental releases may impact general population and environmental exposures. Factors affecting releases include volumes produced, processed and used; numbers of sites; and processes of manufacture, processing, and use.

Based on IUR data, the maximum total number of industrial sites manufacturing, processing, or using these chemicals is confidential.

The following release statements are made based on inferences regarding the non-confidential use information reported in IUR and summarized in Tables 1 and 2.

For CAS# 61790-50-9 and 8050-09-7 the industrial function was reported as "Processing as a reactant:"

Many chemicals designated as reactants have industrial releases that are a relatively low percentage of the volume. Lower percentage releases occur when a high percentage of the chemical reacts without excess loss during its use as an intermediate. The actual percentage and quantity of release of the reported chemical associated with this processing or use are not known.

For CAS# 61790-50-9; 61790-51-0; and 8050-09-7 industrial function was reported as "Processing—incorporation into formulation, mixture, or reaction product:"

Many chemicals designated as product components have industrial releases that are a relatively low percentage of the volume. Lower percentage releases occur when a high percentage of the volume is incorporated at without significant process losses during its incorporation into formulation, mixture, or product. The actual percentage and quantity of release of the reported chemical associated with this processing or use are not known.

For CAS# 61790-51-0 and 8050-09-7 industrial function was reported as "Use—non-incorporative activities"; for CAS# 8050-09-7 industrial function was also reported as "Processing—incorporation into article" and "Not readily obtainable:"

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[20] NIOSH, 1988. OSHA PEL Project Documentation. http://www.cdc.gov/niosh/pel88/npelcas.html. Accessed, 7/11/08.

Chemicals designated for incorporation into articles, "use – non-incorporative activities," or "not readily obtainable" can have variable release percentages during industrial processing and use. The actual percentage and quantity of release of the reported chemical associated with this processing or use are not known.

For CAS# 61790-50-9 and 8050-09-7, IUR reported processing and use as intermediates:

Many chemicals designated as chemical intermediates have industrial releases that are a relatively low percentage of the volume. Lower percentage releases occur when a high percentage of the chemical reacts without excess loss during its use as an intermediate. The actual percentage and quantity of release of the reported chemical associated with use are not known.

For CAS# 61790-50-9; 61790-51-0; and 8050-09-7, IUR also reported one of the following processing and uses:

Chemicals designated to have industrial use as adhesives and binding agents, processing aid, not otherwise listed, process regulators, used in vulcanization or polymerization processes, "other" or "not readily obtainable" can have variable release percentages during industrial processing and use. The actual percentage and quantity of release of the reported chemical associated with these categories are not known.

Experience has shown that air releases due to volatilization have not been an issue for chemicals with vapor pressures below 0.01 torr. These chemicals' vapor pressure is at a level at which air releases may be insignificant for most common handling of liquids at ambient conditions.

Exposures to the General Population and the Environment

Based on the information under the release section above, it is likely that there would be some releases to water or air during manufacturing, processing, and use. A search of additional relevant databases did not provide any further information on releases of this chemical. EPA identifies, for the purposes of risk-based prioritization, a moderate potential that the general population and the environment might be exposed to these chemicals. The IUR ranking for general population and the environment is medium due to the likelihood that there will be exposure to rosin and rosin salts chemicals based on the use codes in the IUR data (see Table 1).

Persistence and bioaccumulation ratings for these chemical are P2 and B1, with the exception of rosin, hydrogenated (CAS No. 65997-06-0), which is P3, B1[21]. These ratings suggest that most rosin and rosin salts are persistent in the environment; and are not very bioaccumulative. Members of this category are expected to biodegrade in the environment slowly. Most compounds will be minimally mobile in soil and will adsorb strongly to solids and sediments in the aquatic environment. Vapor pressures are negligible to low.

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[21] USEPA, 2008. Physical/Chemical and Environmental Fate Characterization for High Production Chemicals, Rosin and Rosin Salts Category.

Based on the information considered, including the fate report, known uses, and the Agency's expert judgment, EPA identifies a moderate potential for exposure to the general population and the environment.

Exposures to Consumers

The non-confidential consumer uses included in the IUR submissions for many of the chemicals in this category are rubber and plastic products. Table 2 at the end of this summary provides additional details.

EPA identifies a high potential for exposures to consumers based on the use of products containing these chemicals.

There is also potential for exposure to consumers based on information from public data sources. Rosin and rosin salts can be used in printing inks, adhesives, chewing gum, coatings, paper, or soap and detergents industries[22]. For CAS# 61790-51-0 and CAS# 8050-09-7, potential exposure to consumers is likely from these chemical found in household products.

EPA identifies a high potential for exposures to consumers from products containing these chemicals based on information from public data sources.

Exposures to Children

Based on non-confidential IUR data, the commercial and consumer uses are rubber and plastic products for many of the rosin and rosin salts chemicals. Children may be potentially exposed to rosin and rosin salts through household use of consumer products containing these chemicals.

EPA identifies a high potential for exposures to children based on the use of products containing these chemicals. One chemical reported yes in uses in products intended to be used by children; one chemical reported that such information was not readily obtainable. One chemical claimed this information to be CBI.

This exposure characterization was completed using both public, non-confidential sources, and one or more IUR submissions that were available as of this writing.

Below are summaries of non-confidential information in the IUR for each of the individual chemicals in this category.

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[22] Pine Chemicals Association, 2004. High Production Volume Final Submission for Rosins and Rosin Salts. September 2004. Accessed 7/11/08 at http://www.epa.gov/HPV/pubs/summaries/rosnsalt/c13134ft.pdf.

Non Confidential IUR Data Summary: CAS# 8050-09-7

Manufacturing/Import Information

Production and import volume:	100 million to 500 million pounds
List of non-CBI companies*:	Aceto Corporation Akzo Nobel Coatings Inc. Akzo Nobel Coatings Inc. Ashland Inc. Bayer Material Science Eastman Chemical Company FRP Services & Co. (America) Inc. Gehring-Montgomery, Inc. Georgia-Pacific Corporation Hercules Incorporated Palmer Holland Inc. Sojitz Corporation of America TR International, Incorporated
Maximum number of exposed workers**:	1,000 or greater (including those of manufacturing, processing and use)
Highest non-CBI concentration:	up to 100% by weight
Non-CBI physical forms*:	dry powder; solid; liquid

* There may be other companies and physical forms that are claimed confidential.
** There may be additional potentially exposed industrial workers that are not included in this estimate since not all submitters were required to report on industrial processing and use and/or there may be at least one use that contains a "Not Readily Obtainable" (NRO) response among the submissions.

Table 1
Industrial Processing and Use Information
Information Reported in 2006 IUR

Processing Activity	Industrial Sector	Function in Industrial Sector
Processing--incorporation into article	Petrochemical Manufacturing	Adhesives and binding agents
Processing as a reactant	Other Basic Organic Chemical Manufacturing	Other
Processing as a reactant	Other Basic Organic Chemical Manufacturing	Not Readily Obtainable
Processing as a reactant	Resin and Synthetic Rubber Manufacturing	Intermediates
Processing as a reactant	Resin and Synthetic Rubber Manufacturing	Other
Processing--incorporation into formulation, mixture, or	Adhesive Manufacturing	Adhesives and binding agents

reaction product		
Processing--incorporation into formulation, mixture, or reaction product	Other Basic Organic Chemical Manufacturing	Intermediates
Processing--incorporation into formulation, mixture, or reaction product	Other Basic Organic Chemical Manufacturing	Other
Processing--incorporation into formulation, mixture, or reaction product	Tire Manufacturing	Processing aid, not otherwise listed
Use--nonincorporative activities	Other Basic Organic Chemical Manufacturing	Adhesives and binding agents
Not Readily Obtainable	Other Miscellaneous Durable Goods Merchant Wholesalers	Not Readily Obtainable
Not Readily Obtainable	Not Readily Obtainable	Not Readily Obtainable
Additional line item(s) may be claimed as CBI		

Table 2
Commercial/ Consumer Uses
Information Reported in 2006 IUR

Commercial/ Consumer Product Category Description	**Highest Maximum Concentration Range**	**Use in Children's Products**
Adhesives and sealants	61% - 90%	Yes
Paints and coatings	1% - 30%	No
Paper products	NRO	No
Rubber and plastic products	Less than 1%	No
Other	1% - 30%	Yes
Not Readily Obtainable	NRO	NRO
Additional line item(s) may be claimed as CBI		

Non Confidential IUR Data Summary: CAS# 61790-51-0

Manufacturing/Import Information

Production and import volume:	1 million to 10 million pounds
List of non-CBI companies*:	Akzo Nobel Coatings Inc. Asphalt Materials, Inc. DuPont Performance Elastomers LLC Flint Hills Resources Hercules Incorporated Heritage Synfuel Binders, LLC
Maximum number of exposed workers**:	1,000 or greater (including those of manufacturing, processing and use)
Highest non-CBI concentration:	up to 100% by weight
Non-CBI physical forms*:	dry powder; solid; liquid

* There may be other companies and physical forms that are claimed confidential.
** There may be additional potentially exposed industrial workers that are not included in this estimate since not all submitters were required to report on industrial processing and use and/or there may be at least one use that contains a "Not Readily Obtainable" (NRO) response among the submissions.

Table 1
Industrial Processing and Use Information
Information Reported in 2006 IUR

Processing Activity	**Industrial Sector**	**Function in Industrial Sector**
Processing--incorporation into formulation, mixture, or reaction product	Other Rubber Product Manufacturing	Process regulators, used in vulcanization or polymerization processes
Use--nonincorporative activities	Other Rubber Product Manufacturing	Processing aid, not otherwise listed
Additional line item(s) may be claimed as CBI		

Table 2
Commercial/ Consumer Uses
Information Reported in 2006 IUR

Commercial/ Consumer Product Category Description	**Highest maximum concentration range**	**Use in Children's Products**
Rubber and plastic products	Less than 1%	No
Additional line item(s) may be claimed as CBI		

Non Confidential IUR Data Summary: CAS# 61790-50-9

Manufacturing/Import Information

Production and import volume:	10 million to 50 million pounds
List of non-CBI companies*:	Akzo Nobel Coatings Inc. DuPont Performance Elastomers LLC Eastman Chemical Company Georgia-Pacific Corporation Hercules Incorporated W.R. Grace, Performance Chemicals
Maximum number of exposed workers**:	1,000 or greater (including those of manufacturing, processing and use)
Highest non-CBI:	up to 100% by weight
Non-CBI physical forms*:	pellets or large crystals; solid; liquid

* There may be other companies and physical forms that are claimed confidential.
** There may be additional potentially exposed industrial workers that are not included in this estimate since not all submitters were required to report on industrial processing and use and/or there may be at least one use that contains a "Not Readily Obtainable" (NRO) response among the submissions.

Table 1
Industrial Processing and Use Information
Information Reported in 2006 IUR

Processing Activity	Industrial Sector	Function in Industrial Sector
Processing as a reactant	Other Basic Organic Chemical Manufacturing	Intermediates
Processing as a reactant	Resin and Synthetic Rubber Manufacturing	Adhesives and binding agents
Processing--incorporation into formulation, mixture, or reaction product	All Other Miscellaneous Manufacturing	Adhesives and binding agents
Processing--incorporation into formulation, mixture, or reaction product	Other Rubber Product Manufacturing	Other
Processing--incorporation into formulation, mixture, or reaction product	Other Rubber Product Manufacturing	Process regulators, used in vulcanization or polymerization processes
Processing--incorporation into formulation, mixture, or reaction product	Residential Building Construction	Adhesives and binding agents
Processing--	Wood Kitchen Cabinet	Adhesives and binding

incorporation into formulation, mixture, or reaction product	and Countertop Manufacturing	agents
Additional line item(s) may be claimed as CBI		

Table 2
Commercial/ Consumer Uses
Information Reported in 2006 IUR

Commercial/ Consumer Product Category Description	Highest Maximum Concentration Range	Use in Children's Products
Rubber and plastic products	Less than 1%	No
Not Readily Obtainable	NRO	NRO
Additional line item(s) may be claimed as CBI		

Non Confidential IUR Data Summary: CAS# 65997-06-0

Manufacturing/Import Information

Production and import volume:	1 million to 10 million pounds
List of non-CBI companies:	Ciba Specialty Chemicals Corp. Eastman Chemical Company Flint Group North America Corporation H.B. Fuller Company Hercules Incorporated
Maximum number of exposed workers:	1,000 or greater (including those of manufacturing, processing and use)
Highest non-CBI concentration:	up to 100% by weight
Non-CBI physical forms:	solid; liquid

* There may be other companies and physical forms that are claimed confidential.
** There may be additional potentially exposed industrial workers that are not included in this estimate since not all submitters were required to report on industrial processing and use and/or there may be at least one use that contains a "Not Readily Obtainable" (NRO) response among the submissions.

Table 1
Industrial Processing and Use Information
Information Reported in 2006 IUR

Processing Activity	Industrial Sector	Function in Industrial Sector
Claimed as CBI		

Table 2
Commercial/ Consumer Uses
Information Reported in 2006 IUR

Commercial/ Consumer Product Category Description	Highest Maximum Concentration Range	Use in Children's Products
Claimed as CBI		

Non Confidential IUR Data Summary: CAS# 68425-08-1

Manufacturing/Import Information

Production and import volume:	<500,000 pounds
List of non-CBI companies*:	Hercules Incorporated
Maximum number of exposed workers**:	between 100 and 999 (including those of manufacturing, processing and use)
Highest non-CBI concentration:	up to 100% by weight
Non-CBI physical forms:	confidential

* There may be other companies that are claimed confidential.
** There may be additional potentially exposed industrial workers that are not included in this estimate since not all submitters were required to report on industrial processing and use and/or there may be at least one use that contains a "Not Readily Obtainable" (NRO) response among the submissions.

Table 1
Industrial Processing and Use Information
Information Reported in 2006 IUR

Processing Activity	Industrial Sector	Function in Industrial Sector
None reported		

Table 2
Commercial/ Consumer Uses
Information Reported in 2006 IUR

Commercial/ Consumer Product Category Description	Highest Maximum Concentration Range	Use in Children's Products
None reported		

Attachment 2 Section I

Home Page > Executive Branch > Code of Federal Regulations > Electronic Code of Federal Regulations

Electronic Code of Federal Regulations
e-CFR™

e-CFR Data is current as of October 2, 2008

Title 40: Protection of Environment

PART 180—TOLERANCES AND EXEMPTIONS FROM TOLERANCES FOR PESTICIDE CHEMICALS IN FOOD

Browse Previous | Browse Next

Subpart D—Exemptions From Tolerances

§ 180.900 Exemptions from the requirement of a tolerance.

An exemption from a tolerance shall be granted when it appears that the total quantity of the pesticide chemical in or on all raw agricultural commodities for which it is useful under conditions of use currently prevailing or proposed will involve no hazard to the public health.

[69 FR 23117, Apr. 28, 2004]

§ 180.905 Pesticide chemicals; exemptions from the requirement of a tolerance.

(a) When applied to growing crops, in accordance with good agricultural practice, the following pesticide chemicals are exempt from the requirement of a tolerance:

(1) [Reserved]

(2) *N* -Octylbicyclo(2,2,1)-5-heptene-2,3-dicarboximide.

(3) Petroleum oils.

(4) Piperonyl butoxide.

(5) [Reserved]

(6) Pyrethrum and pyrethrins.

(7) Rotenone or derris or cube roots.

(8) Sabadilla.

(b) These pesticides are not exempted from the requirement of a tolerance when applied to a crop at the time of or after harvest.

[69 FR 23117, Apr. 28, 2004]

§ 180.910 Inert ingredients used pre- and post-harvest; exemptions from the requirement of a tolerance.

Link to an amendment published at 71 FR 45421, August 9, 2006.

The effective date of the above amendment was delayed in part until August 9, 2009, at 73 FR 45312 and 45316, August 4, 2008.

Residues of the following materials are exempted from the requirement of a tolerance when used in accordance with good agricultural practice as inert (or occasionally active) ingredients in pesticide formulations applied to growing crops or to raw agricultural commodities after harvest:

moles ethylene oxide reacted to produce any product that is a component of the blend shall be either 8, 9, or 40		
Sucrose octaacetate		Adhesive
Sulfite liquors and cooking liquors, spent, oxidized (CAS Reg. No. 68514–09–0)		Surfactant, related adjuvants of surfactants
Sulfuric acid (CAS Reg. No.7664–93–9)	Not to exceed 10% of the pesticide formulation; non-aerosol formulations only	pH Control agent
Synthetic paraffin and its succinic derivatives conforming to 21 CFR 172.275		Carrier, binder, and carrying agent
Synthetic petroleum wax, conforming to 21 CFR 172.888		Binder, carrier, and coating agent
Talc		Solid diluent, carriers
Tall oil; fatty acids not less than 58%, rosin acids not more than 44%, unsaponifiables not more than 8%		Surfactants, related adjuvants of surfactants
Tartrazine		Dye
Terpenes and terpenoids, turpentine oil, alpha-pinene fraction, polymd. (CAS Reg. No. 70750–57–1)		Surfactants, related adjuvants of surfactants
1,1,1,2-Tetrafluoroethane, (CAS Reg. No. 811–97–2)		Aerosol propellant
Tetrahydrofurfuryl alcohol (THFA) (CAS Reg. No 97–99–4)	Expires February 9, 2008	Solvent/cosolvent
α-[*p* -(1,1,3,3-Tetramethylbutyl)phenyl]-ω-hydroxypoly(oxyethylene) produced by the condensation of 1 mole of *p* -(1,1,3,3-tetramethylbutyl)phenol with a range of 1-14 or 30-70 moles of ethylene oxide: if a blend of products is used, the average range number of moles of ethylene oxide reacted to produce any product that is a component of the blend shall be in the range of 1-14 or 30-70		Surfactants, related adjuvants of surfactants
2,4,7,9-Tetramethyl-5-decyn-4, 7-diol	Not more than 2.5% of pesticide formulation	Surfactants, related adjuvants of surfactants
Tetrasodium pyrophosphate		Anticaking agent, conditioning agent
Thiosulfuric acid, disodium salt, anhydrous. (CAS Reg. No 7772–98–7)		Dechlorinator, reducing agent
Thiosulfuric acid, disodium salt,		Do.

[69 FR 23136, Apr. 28, 2004, as amended at 71 FR 30811, May 31, 2006; 71 FR 45423, Aug. 9, 2006; 71 FR 46125, Aug. 11, 2006; 72 FR 51186, Sept. 6, 2007; 73 FR 37858, July 2, 2008; 73 FR 49107, Aug. 20, 2008; 73 FR 53725, Sept. 17, 2008]

§ 180.950 Tolerance exemptions for minimal risk active and inert ingredients.

Unless specifically excluded, residues resulting from the use of the following substances as either an inert or an active ingredient in a pesticide chemical formulation, including antimicrobial pesticide chemicals, are exempted from the requirement of a tolerance under FFDCA section 408, if such use is in accordance with good agricultural or manufacturing practices.

(a) *Commonly consumed food commodities.* Commonly consumed food commodities means foods that are commonly consumed for their nutrient properties. The term commonly consumed food commodities shall only apply to food commodities (whether a raw agricultural commodity or a processed commodity) in the form the commodity is sold or distributed to the public for consumption.

(1) Included within the term commonly consumed food commodities are:

(i) Sugars such as sucrose, lactose, dextrose and fructose, and invert sugar and syrup.

(ii) Spices such as cinnamon, cloves, and red pepper.

(iii) Herbs such as basil, anise, or fenugreek.

(2) Excluded from the term commonly consumed food commodities are:

(i) Any food commodity that is adulterated under 21 U.S.C. 342.

(ii) Both the raw and processed forms of peanuts, tree nuts, milk, soybeans, eggs, fish, crustacea, and wheat.

(iii) Alcoholic beverages.

(iv) Dietary supplements.

(b) *Animal feed items.* Animal feed items means meat meal and all items derived from field crops that are fed to livestock excluding both the raw and processed forms of peanuts, tree nuts, milk, soybeans, eggs, fish, crustacea, and wheat. Meat meal is an animal feed composed of dried animal fat and protein that has been sterilized. Other than meat meal, the term animal feed item does not extend to any item designed to be fed to animals that contains, to any extent, components of animals. Included within the term animal feed items are:

(1) The hulls and shells of the commodities specified in paragraph (a)(2)(ii) of this section, and cocoa bean.

(2) Bird feed such as canary seed.

(3) Any feed component of a medicated feed meeting the definition of an animal feed item.

(c) *Edible fats and oils.* Edible fats and oils means all edible (food or feed) fats and oils, derived from either plants or animals, whether or not commonly consumed, including products derived from hydrogenating (food or feed) oils, or liquefying (food or feed) fats.

(1) Included within the term edible fats and oils are oils (such as soybean oil) that are derived from the commodities specified in paragraph (a)(2)(ii) of this section when such oils are highly refined via a solvent extraction procedure.

(2) Excluded from the term edible fats and oils are plant oils used in the pesticide chemical formulation specifically to impart their characteristic fragrance and/or flavoring.

(d) [Reserved]

(e) *Specific chemical substances.* Residues resulting from the use of the following substances as either an inert or an active ingredient in a pesticide chemical formulation, including antimicrobial pesticide chemicals, are exempted from the requirement of a tolerance under FFDCA section 408, if such use is in accordance with good agricultural or manufacturing practices.

Chemical	CAS No.

Acetic acid, sodium salt	127–09–3
Alpha-cyclodextrin	10016–20–3
Amylopectin, acid-hydrolyzed, 1-octenylbutanedioate	113894–85–2
Amylopectin, hydrogen 1-octadecenylbutanedioate	125109–81–1
Animal glue	None
Ascorbic acid (vitamin C)	50–81–7
Beeswax	8012–89–3
Benzoic acid, sodium salt	532–32–1
Beta-cyclodextrin	7585–39–9
Carbonic acid, monopotassium salt	298–14–6
Carbonic acid, monosodium salt (sodium bicarbonate)	144–55–8
Carnauba wax	8015–86–9
Carob gum (locust bean gum)	9000–40–2
Castor oil	8001–79–4
Castor oil, hydrogenated	8001–78–3
Cellulose	9004–34–6
Cellulose acetate	9004–35–7
Cellulose, carboxy methyl ether, sodium salt	9004–32–4
Cellulose, 2-hydroxyethyl ether	9004–62–0
Cellulose, 2-hydroxypropyl ether	9004–64–2
Cellulose, 2-hydroxypropyl methyl ether	9004–65–3
Cellulose, methyl ether	9004–67–5
Cellulose, mixture with cellulose carboxymethyl ether, sodium salt	51395–75–6
Cellulose, pulp	65996–61–4
Cellulose, regenerated	68442–85–3
Citric acid	77–92–9
Citric acid, 2-(acetyloxy)-, tributyl ester	77–90–7
Citric acid, calcium salt	7693–13–2
Citric acid, calcium salt (2:3)	813–94–5
Citric acid, dipotassium salt	3609–96–9

Citric acid, disodium salt	144–33–2
Citric acid, monohydrate	5949–29–1
Citric acid, monopotassium salt	866–83–1
Citric acid, monosodium salt	18996–35–5
Citric acid, potassium salt	7778–49–6
Citric acid, triethyl ester	77–93–0
Citric acid, tripotassium salt	866–84–2
Citric acid, tripotassium salt, monohydrate	6100–05–6
Citric acid, sodium salt	994–36–5
Citric acid, trisodium salt	68–04–2
Citric acid, trisodium salt, dihydrate	6132–04–3
Citric acid, trisodium salt, pentahydrate	6858–44–2
Coffee grounds	68916–18–7
Dextrins	9004–53–9
1,3-Dioxolan-2-one, 4-methyl-(propylene carbonate)	108–32–7
Fumaric acid	110–17–8
Gamma-cyclodextrin	17465–86–0
Gellan gum	71010–52–1
D-Glucitol (sorbitol)	50–70–4
Glycerol (glycerin) (1,2,3-propanetriol)	56–81–5
Guar gum	9000–30–0
Humic acid	1413–93–6
Humic acid, potassium salt	68514–28–3
Humic acid, sodium salt	68131–04–4
Lactic acid, n-butyl ester	138–22–7
Lactic acid, n-butyl ester, (S)	34451–19–9
Lactic acid, ethyl ester	97–64–3
Lactic acid, ethyl ester,(S)	687–47–8
Lanolin	8006–54–0
Lecithins	8002–43–5
Lecithins, soya	8030–76–0
Licorice Extract	68916–91–6

Maltodextrin	9050–36–6
Paper	None
Potassium chloride	7447–40–7
2-Propanol (isopropyl alcohol)	67–63–0
Red cabbage color, expressed from edible red cabbage heads via a pressing process using only acidified water	None
Silica, amorphous, fumed (crystalline free)	112945–52–5
Silica, amorphous, precipitated and gel	7699–41–4
Silica gel	63231–67–4
Silica gel, precipitated, crystalline-free	112926–00–8
Silica, hydrate	10279–57–9
Silica, vitreous	60676–86–0
Soap (The water soluble sodium or potassium salts of fatty acids produced by either the saponification of fats and oils, or the neutralization of fatty acid)	None
Sorbic acid, potassium salt	24634–61–5
Soapbark (Quillaja saponin)	1393–03–9
Sodium alginate	9005–38–3
Sodium chloride	7647–14–5
Syrups, hydrolyzed starch, hydrogenated	68425–17–2
Ultramarine blue (C.I. Pigment Blue 29)	57455–37–5
Urea	57–13–6
Vanillin	121–33–5
Xanthan gum	11138–66–2

[67 FR 36537, May 24, 2002, as amended at 67 FR 56229, Sept. 3, 2002; 67 FR 78718, Dec. 26, 2002; 68 FR 16437, Apr. 4, 2003; 68 FR 18552, Apr. 16, 2003; 68 FR 52700, Sept. 5, 2003; 69 FR 4077, Jan. 28, 2004; 69 FR 9963, Mar. 3, 2004; 69 FR 29894, May 26, 2004; 69 FR 33578, June 16, 2004; 69 FR 58070, Sept. 29, 2004; 70 FR 7876, Feb. 16, 2005; 70 FR 28447, May 18, 2005; 70 FR 38785, July 6, 2005; 71 FR 30811, May 31, 2006; 73 FR 53725, Sept. 17, 2008]

§ 180.960 Polymers; exemptions from the requirement of a tolerance.

Residues resulting from the use of the following substances, that meet the definition of a polymer and the criteria specified for defining a low-risk polymer in 40 CFR 723.250, as an inert ingredient in a pesticide chemical formulation, including antimicrobial pesticide chemical formulations, are exempted from the requirement of a tolerance under FFDCA section 408, if such use is in accordance with good agricultural or manufacturing practices.

	CAS

Attachment 3, Section 7

Methyl Esters of Tall-Oil Fatty Acids; Tolerance Exemption

[Federal Register: May 29, 1996 (Volume 61, Number 104)]
[Proposed Rules]
[Page 26859-26861]
From the Federal Register Online via GPO Access [wais.access.gpo.gov]
[DOCID:fr29my96-30]

DEC 15 2008

ENVIRONMENTAL PROTECTION AGENCY
40 CFR Part 180
[PP 6E04666/P660; FRL-5371-6]
RIN 2070-AC18

Methyl Esters of Tall-Oil Fatty Acids; Tolerance Exemption

AGENCY: Environmental Protection Agency (EPA).
ACTION: Proposed rule.

SUMMARY: This document proposes that methyl esters of tall-oil fatty acids be exempted from the requirement of a tolerance when used as an inert ingredient (adjuvant) in pesticide formulations. This proposed regulation was requested by Union Camp Corporation pursuant to the Federal Food, Drug, and Cosmetic Act (FFDCA).

DATES: Comments, identified by the docket number [PP 6E04666/P660], must be received on or before June 28, 1996.

ADDRESSES: By mail, submit written comments to: Public Response and Program Resources Branch, Field Operations Division (7506C), Office of Pesticide Programs, Environmental Protection Agency, 401 M St., SW., Washington, DC 20460. In person deliver comments to: Rm. 1132, Crystal Mall #2, 1921 Jefferson Davis Highway, Arlington, VA.

Information submitted as a comment concerning this document may be claimed confidential by marking any part or all of that information as ``Confidential Business Information'' (CBI). Information so marked will not be disclosed except in accordance with procedures set forth in 40 CFR part 2. A copy of the comment that does not contain CBI must be submitted for inclusion in the public record. Information not marked confidential will be included in the public docket by EPA without prior notice. The public docket is available for public inspection in Rm. 1132 at the address given above, from 8 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays.

Comments and data may also be submitted electronically by sending electronic mail (e-mail) to: opp-docket@epamail.epa.gov. Electronic comments must be submitted as an ASCII file avoiding the use of special characters and any form of encryption. Comments and data will also be accepted on disks in WordPerfect in 5.1 file format or ASCII file

Director, Registration Division, Office of Pesticide Programs.

Therefore, it is proposed that 40 CFR part 180 be amended as follows:

PART 180--[AMENDED]

1. The authority citation for part 180 continues to read as follows:

Authority: 21 U.S.C. 346a and 371.

2. In Sec. 180.1001, the table to paragraph (c) is amended by adding alphabetically the inert ingredient ``Methyl esters of tall-oil fatty acids,'' to read as follows:

Sec. 180.1001 Exemptions from the requirements of a tolerance.

* * * * *

Ingredients	Limits	Uses
* * * * * * *		
Methyl esters of tall-oil fatty acids. (Fatty acids not less than 58 percent, rosin acids not less than 44 percent unsaponifiables not less than 8 percent).	....	Adjuvant
* * * * * * *		

[[Page 26861]]

[FR Doc. 96-13441 Filed 5-28-96; 8:45 am]
BILLING CODE 6560-50-F

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1999 1998 1997 1996 1995 1994

format. All comments and data in electronic form must be identified by the docket number, [PP 6E04666/P660]. No CBI should be submitted through e-mail. Electronic comments on this proposed rule may be filed online at many Federal Depository Libraries. Additional information on electronic submissions can be found below in this document.
FOR FURTHER INFORMATION CONTACT: By mail: Bipin Gandhi, Registration Support Branch, Registration Division (7505W), Office of Pesticide Programs, Environmental Protection Agency, 401 M St., SW., Washington, DC 20460. Office location, telephone number, and e-mail address: 2800 Crystal Drive, North Tower, Arlington, VA, (703) 308-8380, e-mail: gandhi.bipin@epamail.epa.gov.

SUPPLEMENTARY INFORMATION: Union Camp Corporation, P.O.Box 2668, Savannah, GA. 31402, has submitted pesticide petition (PP) 6E04666 to EPA requesting that the Administrator, pursuant to section 408(e) of the FFDCA, 21 U.S.C. 346a(e), propose to amend 40 CFR 180.1001(c) by establishing an exemption from the requirement of a tolerance for methyl esters of tall-oil fatty acids when used as an inert ingredient (adjuvant) in pesticide formulations applied to growing crops or to raw agricultural commodities after harvest.

Inert ingredients are all ingredients that are not active ingredients as defined in 40 CFR 153.125 and include, but are not limited to, the following types of ingredients (except when they have a pesticidal efficacy of their own): solvents such as alcohols and hydrocarbons; surfactants such as polyoxyethylene polymers and fatty acids; carriers such as clay and diatomaceous earth; thickeners such as carrageenan and modified cellulose; wetting, spreading, and dispersing agents; propellants in aerosol dispensers; microencapsulating agents; and emulsifiers. The term ``inert'' is not intended to imply nontoxicity; the ingredient may or may not be chemically active.

The data submitted in the petition and other relevant material have been evaluated. As part of the EPA policy statement on inert ingredients published in the Federal Register of April 22, 1987 (52 FR 13305), the Agency set forth a list of studies which would generally be used to evaluate the risks posed by the presence of an inert ingredient in a pesticide formulation. However, where it can be determined without that data that the inert ingredient will present minimal or no risk, the Agency generally does not require some or all of the listed studies to rule on the proposed tolerance or exemption from the requirement of a tolerance for an inert ingredient. The Agency has decided that no data, in addition to that described below, for methyl esters of tall-oil fatty acids will need to be submitted. The rationale for this decision is described below:

(1) Tall-oil fatty acids are exempted from the requirement of a tolerance under 40 CFR 180.1001(c) as ``Tall-oil; fatty acids not less than 58 percent, rosin acids not more than 44 percent, unsaponifiables not more than 8 percent.''

[[Page 26860]]

(2) Methyl esters of tall-oil fatty acids are prepared from tall-oil fatty acids. These methyl esters degrade to tall-oil fatty acids and therefore, are considered no more toxic than the corresponding tall-oil fatty acids.

(3) Methyl esters (distilled) of tall-oil fatty acids contain 1 to 5 percent rosin acids and 2 percent unsaponifiables and are therefore expected to be less toxic compared to the maximum permitted levels of 44 percent rosin acids and 8 percent unsaponifiables respectively for tall-oil fatty acids specified under 40 CFR 180.1001(c).

Based upon the above information and review of its use, EPA has found that, when used in accordance with good agricultural practice, this ingredient is useful and a tolerance is not necessary to protect the public health. Therefore, EPA proposes that the exemption from the requirement of a tolerance be established as set forth below.

Any person who has registered or submitted an application for registration of a pesticide, under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) as amended, which contains any of the ingredients listed herein, may request within 30 days after publication of this document in the Federal Register that this proposal be referred to an Advisory Committee in accordance with section 408(e) of FFDCA.

Interested persons are invited to submit written comments on the proposed regulation. Comments must bear a notation indicating the docket number, [PP 6E04666/P660].

A record has been established for this rulemaking under docket number [PP 6E04666/P660] (including comments and data submitted electronically as described below). A public version of this record, including printed, paper versions of electronic comments, which does not include any information claimed as CBI, is available for inspection from 8 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays. The public record is located in Room 1132 of the Public Response and Program Resources Branch, Field Operations Division (7506C), Office of Pesticide Programs, Environmental Protection Agency, Crystal Mall #2, 1921 Jefferson Davis Highway, Arlington, VA.

Electronic comments can be sent directly to EPA at:
opp-docket@epamail.epa.gov

Electronic comments must be submitted as an ASCII file avoiding the use of special characters and any form of encryption.

The official record for this rulemaking, as well as the public version, as described above will be kept in paper form. Accordingly, EPA will transfer all comments received electronically into printed, paper form as they are received and will place the paper copies in the official rulemaking record which will also include all comments submitted directly in writing. The official rulemaking record is the paper record maintained at the address in ``ADDRESSES '' at the beginning of this document.

The Office of Management and Budget has exempted this proposed rule from the requirements of section 3 of Executive Order 12866.

This action does not impose any enforceable duty, or contain any ``unfunded mandates'' as described in Title II of the Unfunded Mandates Reform Act of 1995 (Pub. L. 104-4), or require prior consultation as specified by Executive Order 12875 (58 FR 58093, October 28, 1993), entitled Enhancing the Intergovernmental Partnership, or special consideration as required by Executive Order 12898 (59 FR 7629, February 16, 1994).

Pursuant to the requirements of the Regulatory Flexibility Act (Pub. L. 96-3 54, 94 Stat. 1164, 5 U.S.C. 601-612), the Administrator has determined that regulations establishing new tolerances or raising tolerance levels or establishing exemptions from tolerance requirements do not have a significant economic impact on a substantial number of small entities. A certification statement to this effect was published in the Federal Register of May 4, 1981 (46 FR 24950).

List of Subjects in 40 CFR Part 180

Environmental protection, Administrative practice and procedure, Agricultural commodities, Pesticides and pests, Reporting and recordkeeping requirements.

Dated: May 16, 1996.

Stephen L. Johnson,

Attachment 4
Section 7

U.S. Environmental Protection Agency
Office of Pesticide Programs
List of Inert Pesticide Ingredients
List 3 - Inerts of unknown toxicity - By Chemical Name
UpdatedAugust 2004

441045-43-8		hydrochloride	3
		Sulfuric acid, monosodium salt, compd. with 1-dodecanami	3
8002-26-4		Tall oil	3
67746-05-8		Tall oil fatty acid isophthalic alkyd	3
		Tall oil fatty acid soap N-C16-18-alkyl trimethylenediame	3
68953-36-6		Tall oil fatty acids, reaction products with tetraethylene pent	3
8052-10-6		Tall oil rosin	3
69278-92-8		Tall oil, calcium zinc salt	3
61789-01-3		Tall oil, epoxidized, 2-ethylhexyl esters	3
68647-71-2		Tall oil, potassium salt	3
65071-95-6		Tall-oil, ethoxylated	3
61791-53-5	N-	Tallow alkyltrimethylenediamines oleates	3
		Tallow bis(2-hydroxyethyl)glycinate	3
68122-54-3		Tallow, ethoxylated	3
8030-78-2		Tallowtrimethylammonium chloride	3
1401-55-4		Tannins	3
87-69-4		Tartaric acid	3
68647-73-4		Tea tree oil	3
68917-71-5		Terpenes and terpenoids, lime oil	3
68647-72-3		Terpenes, orange oil	3
98-55-5	alpha-	Terpineol	3
80-26-2	alpha-	Terpineol acetate	3
58985-18-5		Terpineol, dihydro-, acetate	3
79-34-5	1,1,2,2-	Tetrachloroethane	3
1897-45-6	2,4,5,6-	Tetrachloroisophthalonitrile	3
1191-50-0		Tetradecyl sulfate, sodium salt	3
36366-93-5		Tetraethylene glycol monophenyl ether	3

Attachment 5 section 7

FOOD ADDITIVE STATUS LIST

Formerly called Appendix A of the Investigations Operations Manual (IOM); New items are highlighted in yellow. If you are using an older web browser and you do not see the highlighting, you may download this document in PDF (270 KB) for printing.

Forward | Abbreviations | Color Additive Status List

A B C D E F G H I J K L M N O P Q R S T U V W X Y Z

FOREWORD

This Food Additives Status List organizes additives found in many parts of 21 CFR into one alphabetized list. Additives included are those specified in the regulations promulgated under the FD&C Act, under Sections 401 (Food Standards), and 409 (Food Additives). The list also includes selected pesticide chemicals from 40 CFR 180 for which EPA has set tolerances in food. FDA enforces those tolerances. Within the space available, the Food Additives Status List includes use limitations and permitted tolerances for each additive. For complete information on its use limitations, refer to the specific regulation for each substance. New regulations and revisions are published in current issues of the Federal Register as promulgated. Also refer to the CFSAN website on Food Additives and Premarket Approval to review several FDA databases of additive categories. For example, EAFUS (Everything Added to Food in the United States) is a helpful reference within the limitations described at the beginning of the database.

The Food Additive Status List omits certain categories of additives. Here are the omissions:

1. Obviously safe substances not cited in a regulation as Generally Recognized as Safe (GRAS). You may find such substances on an FDA web site, which contains GRAS notifications received from companies since 1998, and FDA's response.
2. Synthetic flavoring substances in 21CFR 172.515. The CFR does not contain a complete list of permissible flavorings. Certain trade groups such as the Flavor Extract Manufacturers Association have established expert panels to evaluate and make determinations on the GRAS status of their products. If you need help in determining the acceptability of a flavoring after consulting 21 CFR 172.515, contact CFSAN Office of Food Additive Safety (HFS-200) at (301) 436-1200.
3. Those pending administrative determination.
4. Substances granted prior sanction for specific use prior to enactment of the Food Additives Amendment. For additional information on these substances, contact the CFSAN Office of Food Additive Safety (HFS-200) at (301) 436-1200.
5. Indirect food additives, 21 CFR Parts 175, 176, 177, & Part 178 (except that sanitizing agents for food processing equipment as listed in 178.1010 are included in the Food Additives list.) Be aware that as a result of the Food Quality Protection Act of 1996 and Antimicrobial Regulation Technical Corrections Act of 1998, EPA now has jurisdiction over sanitizing solutions applied to permanent or semi-permanent food contact surfaces, other than food packaging. To look up indirect food additives in Parts 175, 176, 177 and 178 go to FDA's "List of Indirect Additives Used in Food Contact Substances". Use it to locate the regulation in which its use is fully described. FDA has recently implemented a new way to market, called "Premarket Notification", for certain food contact substances. These notifications are effective only for the manufacturer or supplier identified in the notification. A list of effective notifications is available on the FDA website.

6. Color additives, 21 CFR Parts 70, 71, 73, 74, 80 & 82. Go to the Color Additives Status List following the Food Additives Status list in Appendix A.

NOTE: The Food Additives Status List is provided only as a quick look-up on the use limitations for a food additive or pesticide chemical. It is possible that mistakes or omissions could have occurred. Additionally, there may be cases where the agency has offered interpretations concerning specific provisions of the regulations. For example, in the case of boiler water additives or other minor ingredients, processing aids, or indirect additives, FDA has not objected, in certain cases, to the substitution of ammonium, calcium, magnesium, potassium, or sodium salts for each other when only one is listed in a regulation. The Food Additive Status list is updated annually, so it may not reflect the latest information. For all these reasons, take care before advising a firm that a use of a particular food additive is prohibited or otherwise limited. Read the actual regulation. If there are any doubts or if a particular situation is unclear, you or your supervisor should consult with the CFSAN, Office of Food Additive Safety (HFS-200) at (301) 436-1200, or the Division of Petition Review (HFS-265) at (301) 436-1264, or the Division of Food Contact Substance Notification Review HFS-275 at (301) 436-1162, or the Division of Biotechnology and GRAS Notice Review HFS-255 at (301) 436-1221.

Please send corrections or additions to the list to Harold Woodall, FDA/CFSAN Office of Food Additive Safety (HFS-206), 5100 Paint Branch Parkway, College Park, Maryland 20740 or e-mail them to harold.woodall@fda.hhs.gov.

Tagetes (marigold) oil - FL/ADJ, REG, GMP, As oil only -172.510

Talc - GRAS - 182.2437 (magnesium silicate)

Tall oil rosin, glycerol ester of - MISC, REG, GMP, Softener for chewing gum - 172.615

Please send corrections or additions to the list to Harold Woodall, FDA/CFSAN Office of Food Additive Safety (HFS-206), 5100 Paint Branch Parkway, College Park, Maryland 20740 or e-mail them to harold.woodall@fda.hhs.gov.

ABBREVIATIONS USED

Technical Effects

Type	Kind, effect or use of additive	Type	Kind, effect or use of additive
AC	Anticaking agent	AF	Antifoaming (or defoaming) agent
AOX	Antioxidant	BC	Boiler compound
BL	Bleaching agent or flour-maturing agent	B&N	Buffer and neutralizing agent
CTG	Component or coating for fruits & vegetables	DS	Dietary supplement
EMUL	Emulsifier	ENZ	Enzyme
ESO	Essential oil and/or oleoresin (solvent free)	FEED	Substances under the Food Additives Amendment added directly to feed
FLAV	Natural flavoring agent	FL/ADJ	Substance used in conjunction with flavors
FUM	Fumigant	FUNG	Fungicide
HERB	Herbicide	HOR	Hormone
INH	Inhibitor	MISC	Miscellaneous
NAT	Natural substances and extractives	NNS	Non-nutritive sweetener
NUTR	Nutrient	NUTRS	Nutritive Sweetener
PEST	Pesticide other than fumigant	PRES	Chemical preservative
SANI	Sanitizing agent for food processing equipment	SDA	Solubilizing and dispersing agent
SEQ	Sequestrant	SOLV	Solvent
SP	Spices, other natural seasonings & flavorings	SP/ADJ	Spray adjuvant
STAB	Stabilizer	SY/FL	Synthetic flavor
VET	Veterinary drug, which may leave residue in edible tissues of animals or in edible animal products		

Status

Type	Kind, effect or use of additive	Type	Kind, effect or use of additive
BAN	Substances banned prior to the Food Additives Amendment (FAA) because of toxicity. These substances are bolded and italicized.	FS	Substances permitted as optional ingredient in a standardized food
GRAS	Generally recognized as safe. Substances in this category are by definition, under Sec. 201(s) of the FD&C Act, not food additives. Most GRAS substances have no quantitative restrictions as to use, although their use must conform to good manufacturing practices. Some GRAS substances, such as	GRAS/FS	Substances generally recognized as safe in foods but limited in standardized foods where the standard provides for its use.

	sodium benzoate, do have a quantitative limit for use in foods.		
ILL	Substances used or proposed for use as direct additives in foods without required clearance under the FAA. Their use is illegal. These substances are bolded and italicized.	PD	Substances for which a petition has been filed but denied because of lack of proof of safety. Substances in this category are illegal and may not be used in foods.
PS	Substances for which prior sanction has been granted by FDA for specific uses. There are a number of substances in this category not listed herein because they have not been published in the FEDERAL REGISTER.	REG	Food additives for which a petition has been filed and a regulation issued.
REG/FS	Food additives regulated under the FAA and included in a specific food standard.		

Attachment 6, section 7.

SANCO Doc 3010.

DEC 15 2008

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1163 Substances (918 exist, 98 other, 146new)	Cipac	Category	List	Annex I 91/414	Legislation	Remarks	#	RMS	Assess Risk?	MRLs Reg 396/2005	MRLs Codex?	mg/kg bw/d	Source/Year	ARfD mg/kg bw/d	Source/Year	Other toxicological evaluations/ remarks
PART A: EXISTING ACTIVE SUBSTANCES DIVIDED INTO FOUR LISTS FOR PHASED EVALUATIONS																
2,4-D	0001	HB, PG	1	In	01/103/EC		1	EL	COM	Reg 149/2008	Yes	0.05	Dir 01/103	not appl.	Dir 01/103	ARfD unnecessary ADI 0,01 JMPR 2001
2,4-DB	0083	HB	1	In	03/31/EC		2	EL	COM	Reg. 149/2008		0.02	Dir 03/31	not appl.	Dir 03/31	ARfD 0.004 AUS 1995
Alpha-Cypermethrin (aka alphamethrin)	0454	IN	1	In	04/58/EC		3	B	COM	Reg 839/2008, Reg. 149/2008		0.015	Dir 04/58	0.04	Dir 04/58	ARfD 0.015 EMEA 1999; 0.02 JECFA 1996
Amitrole (aminotriazole)	0090	HB	1	In	01/21/EC		4	FR	COM	Reg. 149/2008		0.001	Dir 01/21	not appl.	Dir 01/21	ADI 0.002 JMPR 1998, ARfD 0.0003 AUS 1984
Benalaxyl	0416	FU	1	In	04/58/EC		5	PT	COM	Reg. 839/2008, Reg 149/2008	Yes	0.04	Dir 04/58	not appl.	Dir 04/58	ARfD 0.05 AUS 1988 & JMPR 1987
Bentazone	0366	HB	1	In	00/68/EC		6	DE	COM	Reg 149/2008	Yes	0.1	Dir 00/68	0.25	Dir 00/68	ADI 0.1, ARfD unnecessary JMPR 2004
Beta-Cyfluthrin	0482	IN	1	In	03/31/EC		7	DE	COM	Reg. 839/2008, Reg 149/2008	Yes	0.003	Dir 03/31	0.02	Dir 03/31	ADI: 0.04, ARfD. 0.04: JMPR 2006
Bromoxynil	0087	HB	1	In	04/58/EC		8	FR	COM	Reg. 149/2008		0.01	Dir 04/58	0.04	Dir 04/58	

1163 Substances **(918 exist, 98 other, 146new)**	Cipac	Category	List	Annex I 91/414	Legislation	Remarks	#	RMS	Assess Risk?	MRLs Reg 396/2005	MRLs Codex?	ADI mg/kg bw/d	Source/Year	ARfD mg/kg bw/d	Source/Year	Other toxicological evaluations/ remarks
Putrescine (1,4-Diaminobutane))		AT	4B	In		Voted SCoFCAH October 08 (criteria Annex VI Reg. 1490/2002)	44	AT		Reg 839/2008						
Pyrethrins	32	IN	4A	In		Voted SCoFCAH October 08 (criteria Annex VI Reg. 1490/2002)	45	IT								
Quartz sand		RE	4A	In		Voted SCoFCAH October 08 (criteria Annex VI Reg. 1490/2002)	46	AT		Reg. 839/2008						
Repellents by smell/Fish oil			4A	In		Voted SCoFCAH October 08 (criteria Annex VI Reg. 1490/2002)	47	EL		Reg 839/2008						
Repellentsby smell/Sheep fat			4A	In		Voted SCoFCAH October 08 (criteria Annex VI Reg. 1490/2002)	48	EL		Reg 839/2008						
Repellents by smell/ Tall oil crude (CAS 8002-26-4)			4A	In		Voted SCoFCAH October 08 (criteria Annex VI Reg. 1490/2002)	49	EL		Reg. 839/2008						
Repellents by smell/Tall oil pitch (CAS 8016-81-7)			4A	In		Voted SCoFCAH October 08 (criteria Annex VI Reg. 1490/2002)	50	EL		Reg 839/2008						
Sea-algae extract (formerly sea-algae extract and seaweeds)		PG	4A	In		Voted SCoFCAH October 08 (criteria Annex VI Reg. 1490/2002)	51	IT		Reg 839/2008						
Sodium aluminium silicate		RE	4A	In		Voted SCoFCAH October 08 (criteria Annex VI Reg. 1490/2002)	52	HU		Reg 839/2008						
Sodium hypochlorite		BA	4F	In		Voted SCoFCAH October 08 (criteria Annex VI Reg. 1490/2002)	53	NL								
Straight Chain Lepidoptera Pheromones:		AT	4B	In		Voted SCoFCAH October 08 (criteria Annex VI Reg. 1490/2002)	54	AT								
Dodecyl acetate		AT	4B	In		acetate group		AT								

Attachment 7, section 7

U. S. Food and Drug Administration
Center for Food Safety & Applied Nutrition
Office of Premarket Approval

Agency Response Letter
GRAS Notice No. GRN 000039

DEPARTMENT OF HEALTH & HUMAN SERVICES Public Health Service

Food and Drug Administration
Washington, DC 20204

April 24, 2000

Judith A. Weinstein
Novartis Consumer Health, Inc.
560 Morris Avenue
Building F
Summit, NJ 07901-1312

DEC 15 2008

Re: GRAS Notice No. GRN 000039

Dear Ms. Weinstein:

The Food and Drug Administration (FDA) is responding to the notice, dated January 28, 2000, that you submitted in accordance with the agency's proposed regulation, proposed 21 CFR 170.36 (62 FR 18938; April 17, 1997; Substances Generally Recognized as Safe (GRAS); the GRAS proposal). FDA received your notice on January 28, 2000 and designated it as GRAS Notice No. GRN 000039.

The subject of your notice is tall oil phytosterols. The notice informs FDA of the view of Novartis Consumer Health, Inc. (Novartis) that tall oil phytosterols are GRAS, through scientific procedures, for use as a nutrient in vegetable oil spread to reduce the absorption of cholesterol from the gastrointestinal tract at a level up to 12% free phytosterols.

Identity, method of manufacture, and specifications

Your notice describes the manufacturing process for tall oil phytosterols, which are extracted from tall oil soap (a by-product of the pulping process used for coniferous trees in North America and Europe) using organic solvents. The extracted phytosterols are subjected to a complexation-washing process that removes the bulk of the organic material, and the crude phytosterols are then dissolved in alcohol and crystallized. The resulting product, tall oil phytosterols, is predominantly a mixture of four phytosterols (i.e., sitosterol, sitostanol, campesterol, and campestanol). Your notice includes food grade specifications for tall oil phytosterols.

Dietary exposure

According to your notice, the major components of tall oil phytosterols already are present in other vegetable oil based spreads that have a similar intended use.(1) For this reason, you assert that the ingredient tall oil phytosterols provides an additional choice for consumers seeking to maintain a healthy cholesterol level through the consumption of vegetable oil spread. Thus, the intended use of tall oil phytosterols is a substitutional use that would not increase dietary exposure to its main components.

Report of Novartis' "GRAS Panel"

The notice includes the findings of a panel of individuals (Novartis' GRAS panel) who evaluated the data and information that are the basis for Novartis' GRAS determination. Novartis considers the members of its GRAS panel to be qualified by scientific training and experience to evaluate the safety of substances added to food.

In its report, Novartis' GRAS panel compares the composition of tall oil phytosterols to that of the two related ingredients, i.e., vegetable oil sterol esters and plant stanol esters. This comparison includes the levels of the major component phytosterols and phytostanols, the levels of minor phytosterol-like components, and the chemical form of the phytosterols and phytostanols (i.e., whether they are esterified). Novartis' GRAS panel finds that the composition of tall oil phytosterols is intermediate between that of vegetable oil sterol esters and plant stanol esters, and notes that the ester forms that are present in vegetable oil sterol esters and plant stanol esters are rapidly de-esterified *in vivo*.

Novartis' GRAS panel also considers that the level of use of tall oil phytosterols in vegetable oil-based spreads is similar to that of the phytosterol and phytostanol components of vegetable oil sterol esters and plant stanol esters. Novartis' GRAS panel further considers that the intended use of tall oil phytosterols as a nutrient in vegetable oil spread to reduce the absorption of cholesterol from the gastrointestinal tract is similar to that of vegetable oil sterol esters and plant stanol esters.

Given the similarities between the composition, level of use, and intended use of tall oil phytosterols compared to that of the related substances, vegetable oil sterol esters and plant stanol esters, Novartis' GRAS Panel concludes that the intended use of tall oil phytosterols does not raise safety questions. In addition, Novartis' GRAS panel asserts that the potential that the use of tall oil phytosterols would have adverse nutritional effects (i.e., on the uptake of fat-soluble vitamins) has been addressed and adequately resolved in the course of the determinations that vegetable oil sterol esters and plant stanol esters are GRAS.

Novartis' GRAS panel concludes that tall oil phytosterols are GRAS, through scientific procedures, when used in vegetable oil-based spreads to help maintain a healthy cholesterol level, provided that the tall oil phytosterols meet the specifications cited in its report and are used in accordance with current good manufacturing practice in an amount not to exceed 12% phytosterol plus phytostanol in the finished product.

Data and information that Novartis describes to support its GRAS determination

Your notice describes a series of studies conducted with free phytosterols, vegetable oil sterol esters, plant stanol esters, or tall oil phytosterols. In general, you rely on published studies conducted with free phytosterols, vegetable oil sterol esters, or plant stanol esters to determine that the major components of tall oil phytosterols are GRAS. To corroborate this determination, you describe unpublished studies conducted with tall oil phytosterols.

Conclusions

Based on the information provided by Novartis, as well as other information available to FDA, the agency has no questions at this time regarding Novartis' conclusion that tall oil phytosterols are

GRAS under the intended conditions of use. The agency has not, however, made its own determination regarding the GRAS status of the subject use of tall oil phytosterols. As always, it is the continuing responsibility of Novartis to ensure that food ingredients that the firm markets are safe, and are otherwise in compliance with all applicable legal and regulatory requirements.

In accordance with proposed 21 CFR 170.36(f), a copy of the text of this letter, as well as a copy of the information in your notice that conforms to the information in proposed 21 CFR 170.36(c)(1), is available for public review and copying on the Office of Premarket Approval's homepage on the World Wide Web.

Sincerely,
/s/
Alan M. Rulis, Ph.D.
Director
Office of Premarket
Approval
Center for Food Safety
and Applied Nutrition

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(1)In a submission dated January 11, 1999, Lipton informed FDA of its view that vegetable oil sterol esters are GRAS for use in vegetable oil spreads at levels up to 20% to supplement the nutritive value of the spread, and to help structure the fat phase and reduce the fat and water content of the spread. According to Lipton, the use of vegetable oil sterol esters in vegetable oil-based spreads was intended to help maintain healthy cholesterol levels as part of a diet low in saturated fat and cholesterol.

In a submission dated February 18, 1999, McNeil Consumer Healthcare informed FDA of its view that plant stanol esters are GRAS for use as a nutrient in spread at a level of 1.7 grams of plant stanol esters per serving of spread. According to McNeil, the use of plant stanol esters was intended as a nutrient in food to reduce the absorption of cholesterol from the gastrointestinal tract.

Home	**Return to the GRAS Notice Table**			

Content last updated by mdp on 2000-APR-27
Hypertext last updated by mdp on 2000-APR-27

Attachment 8, section 7
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FOOD STANDARDS Australia New Zealand
Te Mana Kounga Kai – Ahitereiria me Aotearoa

FSANZ Home > Standards Development > Applications > Application A417 - Tall oil non-esterified phytosterols as novel food ingredients >

APPLICATION A417 - TALL OIL NON-ESTERIFIED PHYTOSTEROLS

DERIVED FROM TALL OILS

10 October 2001

05/02

DRAFT ASSESSMENT

(Full Assessment - section 15)

Full Report [pdf 358kb]

EXECUTIVE SUMMARY

Background

An Application was received from Novartis Consumer Health Australasia Pty Ltd on

5 June 2000 to amend Standard A19 of the Australian *Food Standards Code* (now known as Volume 1 of the *Food Standards Code*) to approve the use of tall oil non-esterified phytosterols derived from tall oils as Novel Food ingredients in a broad range of products.

Since receiving the Application, Volume 2 of the *Food Standards Code* was gazetted in Australia and New Zealand, consequently Standard 1.5.1- Novel Foods in Volume 2 of the *Food Standards Code* will also require an amendment to approve the use of tall oil non-esterified phytosterols derived from tall oils as Novel Food ingredients.

The Applicant further amended the Initial Application on three subsequent occasions - reducing the range of products in which the use of tall oil non-esterified phytosterols derived from tall oils were sought to be approved. Details specifying the amendments to the Initial Application by the applicant are contained in **Attachment 7** to this Draft Assessment. The final Application amendment occurred on 22 August 2001, and sought approval for the use of tall oil non-esterified phytosterols in edible table-spreads only, at a level of 8%(w/w).

For convenience in this Draft assessment tall oil non-esterified phytosterols derived from tall oils will be referred to as tall oil phytosterols (TOPs).

TOPs are extracted from tall oil soap, a by-product of the pulping process used for coniferous trees and then purified in a three-step process. The free phytosterols are structurally related to cholesterol and occur naturally at low levels (up to 0.9%) in common vegetable oils. TOPs are reported to reduce plasma cholesterol levels.

Under Standards A19 and 1.5.1 of the *Food Standards Code*, for a food to be considered novel it must be a non-traditional food, as defined in the Standard. TOPs are considered to be Novel Foods for the purposes of the Standards because they are non-traditional foods that do not have a history of significant human consumption by the broad community to enable safe use of this food in the form or context in which they are proposed to be presented.

During the Draft Assessment (Full assessment - section 15) period evaluations were performed on the safety of TOPs, estimated dietary exposure for mean and high level consumers and an assessment of the likely implications for consumers, industry, and government agencies if approval for use of TOPs as a Novel Foods ingredient is granted.

Consequently in this Application it is proposed that TOPs be added to edible oil spreads only, at a level of 8% (w/w). Phytosterol esters are currently being used in table-spread products following a recent approval as novel foods in June 2001 by the Ministerial Council.

Issues addressed

Current and proposed use

In the USA, vegetable oil-based spreads containing TOPs at a level up to 12 % have self-affirmed Generally Recognised As Safe (GRAS) status. In the European Union, an application for use in table-spreads is being considered under the Novel Food legislation.

TOPs cannot be used in foods by virtue of clause 2 of Standard A19 and Standard 1.5.1 (Volume 1 and Volume 2 of the *Food Standards Code* respectively). This clause specifies that a novel food must not be sold by way of retail sale as a food or for use as a food ingredient unless it is listed in the table to clause 2 of the above Standards, and complies with the conditions of use, if any specified in the table. The above prohibition came into force on 16 June 2001. At present the only novel food that has been approved for inclusion in the Novel Food Standards are Phytosterol esters (which have specific conditions of use).

The Applicant originally sought permission to use TOPs as Novel Food ingredients in a broad range of foods. Following discussions and correspondence with the Applicant in relation to the available data, the Applicant amended the application on a number of occasions (details of amendments to the initial application are contained in Attachment 7). The final amendment to the initial Application, by the applicant, occurred on 22 August 2001 in which the applicant sought to limit the permission for the use of TOPs in:

- Edible oil spreads (less than 80% fat) at a maximum of 8% (w/w).

Safety evaluation

The safety of TOPs has been evaluated in animals and well as in humans. The available animal studies on TOPs indicate that these substances are poorly absorbed from the gastrointestinal tract, have low toxicity, are not genotoxic and demonstrate no reproductive or developmental toxicity. There was also no evidence of oestrogenic activity in the *in vitro* and *in vivo* studies evaluated.

The studies provided by the Applicant can be used to demonstrate the safety of TOPs up to and including a level of 3.6g/day (i.e. total exposure to TOPs, irrespective of the particular food matrix). There is no evidence of adverse health effects in the human studies, apart from some minor non-significant reductions in vitamin A at doses of 0.9, 1.8 and 3.6g/day without a dose-relationship. There is, however, a decrease in the plasma levels of carotenoids as a result of exposure to TOPs in a milk-based beverage at the highest dose (3.6g/day) over a 4-week period. While the decrease in carotenoid levels observed following exposure is well within the natural variation of carotenoid levels in humans, and not considered to be a concern *per se*, there is a paucity of data on the potential effect on plasma carotenoids at higher levels of TOPs exposure.

Estimated dietary exposure

Dietary modelling was conducted on the proposed uses of TOPs in spreads to determine the dietary intakes for the mean and the 95th percentile consumers (Australian and New Zealand consumers). The maximum level of exposure for a consumer in the target group of 40 years and above was the following:

- Mean consumers (1.3g/day Australian consumers; 1g/day New Zealand consumers) and 95th percentile consumption (3.5 g/day Australian consumers; 2.8 g/day New Zealand consumers).

Effect on cholesterol absorption

The effectiveness of TOPs incorporated into food products to reduce cholesterol absorption has not been specifically assessed as part of this Application, although the human studies that have been examined do provide some information in this regard. Total plasma cholesterol was reduced by 5-7% and Low Density Lipoprotein (LDL) by 5-14% at a dosage of 1.5g/day with a vegetable oil matrix (10-days); 9% and 14% respectively with margarine at 1.5g/day (30-days); 4% and 3% with a cereal bar at 1.8g/day (8-weeks) and; 9% and 13% respectively with a milk based beverage at 3.6 g/day (4-weeks).

Advice to consumers

With phytosterol enriched foods, there is a clear intention to market the reported beneficial effects of TOPs on blood cholesterol and therefore it is important that these foods be consumed as part of a healthy and varied diet that is low in saturated fats and high in fruit and vegetables (by virtue of potential to reduce plasma carotenoid levels). A mandatory advisory statement to this effect is proposed.

There is also a need to protect at-risk groups (children, pregnant and lactating women) in relation to any potential reduction in plasma carotenoid levels as a result of phytosterol intake, although there are limited effects noted from available studies in humans with TOPs. Additionally, in these groups it may not be generally appropriate to reduce cholesterols levels without medical supervision. A mandatory advisory statement indicating that TOP-enriched foods are not recommended for these groups is also proposed.

The use of phytosterol containing spreads should not be considered a substitute for cholesterol-lowering medication and a mandatory advisory statement is proposed that will indicate the need for consumers on such medication to seek medical advice regarding the use of the product in conjunction with their medication. In relation to the ability of phytosterols to reduce cholesterol absorption, this will be considered in the light of the current review of the framework for health claims.

Conclusions

Overall, the data supports the safety of TOPs at the level of intake, which would be achieved by their addition to edible oil spreads at 8% (w/w).

The conclusions from the risk assessment are as follows:

- There is no public health and safety concern associated with the use of TOPs in edible oil spreads at a maximum concentration of 8% (w/w).
- There is some evidence from the available data that TOPs, when incorporated into edible oil spreads at 8% (w/w), can reduce the level of plasma cholesterol in humans.
- Mandatory advisory statements are required to ensure that consumers use phytosterol enriched edible oil spreads appropriately.
- The proposed changes to Volume 1 and Volume 2 of the *Food Standards Code* are consistent with the section 10 objectives of the *Australia New Zealand Food Authority Act* 1991 and the Regulatory Impact Assessment.

Recommendations arising from the Risk Assessment and Regulatory Impact Analysis

On the basis of the available data on the safety of TOPs, permission should not be broadened to foods other than edible oil spreads at this stage. The level in edible oil spreads should be limited to 8% (w/w). TOP preparations must also comply with the established specifications. This approach is consistent with the conclusions of the regulatory impact assessment.

In order to ensure that edible oil spreads containing TOPs are used appropriately by consumers the following mandatory advisory statements should be used:

- *A mandatory advisory statement to the effect that the product should be consumed in moderation as part of a diet low in saturated fats and high in fruit and vegetables.*
- *A mandatory advisory statement to the effect that the product is not recommended for infants, children, and pregnant or lactating women.*
- *A mandatory advisory statement to the effect that consumers on cholesterol-lowering medication should seek medical advice about using the product in conjunction with their medication.*

Full Report [pdf 358kb]

Attachment 9
Section 7.

Environmental and Workplace Health

Substances in Cosmetics and Personal Care Products Regulated Under the Food and Drugs Act (F&DA) That Were In Commerce between January 1, 1987 and September 13, 2001

PDF Format

Help on accessing alternative formats, such as PDF, MP3 and WAV files, can be obtained in the alternate format help section.

Below is a list of those substances found in cosmetics and personal care products that have been identified, through a database search, by Health Canada officials as having been on the Canadian market between January 1, 1987, and September 13, 2001. This substance list will be screened to select those substances that may require priority assessment under CEPA and the NSNRs due to their potential toxicity, bio-accumulation, or persistence. For those substances that do not require priority assessment, they will be prioritized for future assessment under the new environmental assessment regulations. Health Canada will continue to add substances to this list as they are identified in various internal databases.

DEC 15 2008

This list contains ingredients for which no CAS numbers have been found.

To find a particular substance in this list, press "Ctrl+F" in either the HTML or PDF version to display the "FIND" window.

Ingredient Description

COIX LACRYMA-JOBI (JOB'S TEARS) SEED EXTRACT
FIBRONECTIN
IMPERATA CYLINDRICA ROOT EXTRACT
RAHNELLA / SOY PROTEIN FERMENT
ECHIUM PLANTAGINEUM SEED OIL
MARITIME PINE OIL
POPPY PETAL EXTRACT, RED
INFUSION OF PASSIONFLOWER
CINNAMON WOOD
NATURAL BORNEOL EXTRACT, CRYSTALIZED
PETIT GRAIN PARAGUAY OIL
HYDROLYZED RNA
LYSINE HYDROXYPROPYLTRIMONIUM CHLORIDE
BARLEY WATER
COPPER DISODIUM EDETATE
QUILLAJA
RED CLOVER
WHOLE RED CLOVER
RED CLOVER BLOSSOM EXTRACT
LINSEED EXTRACT
LOVAGE ROOT POWDER
CHINESE LOVAGE FLOWERS EXTRACT
SAGE FLOWER
SAGE POWDER
SODIUM CARBONATE, ANHYDROUS
SODIUM CARBONATE, EXSICCATED
ARNICA FLOWERS
ARNICA FLOWERS EXTRACT

GRANULATED PEACH KERNEL
UVEDALIA EXTRACT
MAGNESIUM HVP/HAP CHELATE
CALCIUM HVP/HAP CHELATE
ZINC HVP/HAP CHELATE
COPPER HVP/HAP CHELATE
SOY POWDER
JUJUBE
JUBUBA POWDER
PEAT MOSS
SODIUM TALL OIL SOAP
METHYACRYLIC ACID
CATECHU BLACK EXTRACT
RESINA LARICIS RESIN
STANNUM METALLICUM
GRAPHITES
NARDOSTACHYS JATAMANSI
TRIOLEIN PEG-6
BLACK MALVA EXTRACT
RED WINE EXTRACT
ACACIA EXTRACT
TEA-LAUROYL COLLAGEN AMINO ACIDS
IRON OXIDE YELLOW (AND) IRON OXIDE BROWN
GUIZOTIA ABYSSINICA
1(3H)-FURANONE, 5-HERYLDEYCH 0
MIXED FRUIT ACIDS
POLYSILOXANE POLYALKYLENE COPOLYMER
MESENCHYME EXTRACT
BOVINE MESENCHYME EXTRACT
C12-13 ALCOHOLS BENZOATE
PPG-13 STEARYL ETHER
STEARETH-22
LUNG EXTRACT
ETHYL ACRYLATE/METHACRYLATE COPOLYMER
ROSE HIPS SEED OIL

CANDIDA BOMBICOLA/METHYL MYRISTATE FERMENT
KUKUI LEAF EXTRACT
COCONUT MILK EXTRACT
CHINESE GOLDEN THREAD EXTRACT
SPHINGOLIPID LIPOSOMES
GLYCERETH-7 LACTATE
ACRYLATES/OCTYL ACRYLATE COPOLYMER
RADISH (RAPHANUS SATIVUS) EXTRACT
ALGAE PEPTIDES
ALKYL MODIFIED TRISILOXANE
CHICKPEA FLOUR
DISTILLED TALL OIL FATTY ACID (AND) POTASSIUM SALT
COCO PHOSPHATIDYL PG-DIMONIUM CHLORIDE
SODIUM THREONATE
HOLLY (ILEX AQUIFOLIUM) EXTRACT
ESSENTIAL OIL OF MINT
PEG-5
SODIUM LAURYL ETHER SULFATE
POLYGLYCERYL-2 SESQUIOLEATE
DIMETHICONE COPOLYOL BEESWAX
SILICUM AMINOCHELATE
POTASSIUM POLYSORBATE
PPG-3 HYDROXYETHYL LINOLEAMIDE
NYMPHAEA ALBA ROOT EXTRACT
POLYALDO 1-1-O
ETHOXYLATED GLYCEROL SORBITAN SATURATED FATTY ACID ESTERS
GROUND ANISE SEEDS
GROUND FENNEL SEEDS
DRIED ROSEMARY LEAVES
CALENDULA PETALS INFUSION
GRATED SOAP
KIWI SEED OIL
INFUSION OF GINSENG,GINKGO BILOBA,ECHINACEA,BEE
POLLEN,SPIRULINA,GRAPESEED,PASSIONFRUIT,BANANA
INFUSION OF . . .PINEAPPLE,GUAVA,RICE BRAN, SOYBEAN (SEE 7555)
HYDRATED ALUMINUM MAGNESIUM SILICATE

Pest Management Regulatory Agency
Agence de réglementation de la lutte antiparasitaire

Regulatory Note REG2005-01

PMRA List of Formulants

This Regulatory Note contains a revised list of formulants that are found in pest control products currently registered in Canada under the *Pest Control Products Act* and Regulations. The list reflects the addition of new formulants and the deletion of formulants no longer found in registered pest control products. This document replaces Regulatory Note REG2004-01, *PMRA List of Formulants*.

The list of formulants is also available electronically on the PMRA website and this list will be updated regularly.

NOTE: The new *Pest Control Products Act* (PCPA) was given Royal Assent on December 12, 2002. Paragraph 43(5)(*b*) of the new PCPA indicates that a list of formulants and contaminants that are considered to be of health or environmental concern will be established. This list will contain all of the formulants on lists 1 and 2 of this Regulatory Note, as well as the formulants that are allergens known to cause anaphylactic-type reactions, as indicated in Section 4.14 of Regulatory Directive DIR2004-01, *Formulants Program*, and contaminants of concern found in pesticide active ingredients. The list will be published in the *Canada Gazette* and posted on the PMRA website. Once the new Act is in force, the identity and concentration in a product of any formulant or contaminant on the list will not be confidential and will be available to the public on request.

(publié aussi en français) **31 March 2005**

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Appendix I PMRA Consolidated List of Formulants Sorted by CAS Number

CAS No.	Formulant Names	List No.
000050-70-4	Sorbitol	4A
000050-81-7	L-Ascorbic acid	4A
000050-99-7	Dextrose	4A
000052-51-7	2-Bromo-2-nitro-propane-1,3-dio	3
000054-21-7	Sodium salicyate	3
000056-81-5	Glycerol	4A
000057-10-3	Hexadecanoic acid	4A
000057-11-4	Stearic acid	4A
000057-13-6	Urea	4A
000057-50-1	Sugar	4A
000057-55-6	Propylene glycol	4B
000058-95-7	Vitamin E acetate	3
000060-00-4	Ethylenediaminetetraacetic acid	3
000060-29-7	Ethane, 1,1'-oxybis-	3
000060-33-3	Linoleic acid	3
000061-73-4	C.I. Basic Blue 9	3
000063-42-3	D-(+)-Lactose	4A
000064-02-8	Ethylenediaminetetraacetic acid, tetrasodium salt	3
000064-17-5	Ethanol	4B
000064-19-7	Acetic acid	4B
000065-85-0	Benzoic acid	4B
000066-71-7	1,10-Phenanthroline	3
000067-48-1	Choline chloride	4B
000067-56-1	Methyl alcohol	3
000067-63-0	2-Propanol	4B
000067-64-1	Acetone	3
000067-68-5	Dimethyl sulfoxide	3
000068-04-2	Citric acid, trisodium salt	4A
000068-12-2	Dimethyl formamide	1
000071-23-8	n-Propanol	4B
000071-36-3	1-Butanol	4B
000074-87-3	Methyl chloride	3
000074-98-6	Propane	3
000075-07-0	Acetaldehyde	3
000075-28-5	Isobutane	3
000075-31-0	Isopropylamine	3
000075-37-6	1,1-Difluoroethane	2
000075-52-5	Nitromethane	2

CAS No.	Formulant Names	List No.
008042-47-5	White mineral oil (petroleum)	4A
008047-99-2	N-Ethyltoluenesulfonamide	3
008050-09-7	Rosin	3
008050-15-5	Resin acids and rosin acids, hydrogenated, Me esters	3
008050-26-8	resin acids and rosin acids, esters with pentaerythritol	3
008050-81-5	Simethicone	3
008051-30-7	Coconut oil, reaction products with diethanolamine	3
008052-10-6	Tall oil rosin	3
008052-35-5	Molasses	4A
008052-41-3	Stoddard solvent	2
008052-42-4	Asphalt	3
008052-48-0	Sodium tallow soap	4B
008052-50-4	Tallow, sulfated, sodium salt	3
008061-51-6	Lignosulfonic acid, sodium salt	4B
008061-52-7	Lignosulfonic acid, calcium salt	4B
008061-53-8	Lignosulfonic acid, ammonium salt	3
008068-05-1	Lignin, alkali	3
009000-01-5	Gum arabic	4B
009000-07-1	Carrageenan	4A
009000-28-6	Ghatti gum	3
009000-30-0	Guar gum	4A
009000-40-2	Carob gum (locust bean gum)	4A
009000-59-3	Shellac	3
009000-65-1	Gum tragacanth	3
009000-70-8	Gelatin	4B
009000-71-9	Casein*	4B
009002-18-0	Agar	3
009002-84-0	Polytetrafluoroethylene	3
009002-86-2	Polyvinyl chloride resin	4B
009002-88-4	Polyethylene	4A
009002-89-5	Polyvinyl alcohol	4B
009002-92-0	Polyoxyethylene dodecyl mono ether	4B
009002-93-1	Polyoxyethylene 4-(1,1,3,3-tetramethylbutyl)phenyl ether	3
009003-01-4	Acrylic acid polymer	4B
009003-04-7	Acrylic acid polymer, sodium salt	4B
009003-05-8	Polyacrylamide	4B
009003-07-0	Polypropylene	4B
009003-11-6	Polyoxyethylene-polyoxypropylene copolymer	4B
009003-13-8	Butoxypropylene glycol	3

CAS No.	Formulant Names	List No.
061789-40-0	N-(Coco alkyl) amido propyl dimethyl betaine	3
061789-70-6	Benzenemethanaminium, N-(3-aminopropyl)-N,N-dimethyl-, N-coco acyl derivatives, chlorides	3
061789-77-3	Quaternary ammonium compounds, di(cocoalkyl)dimethyl, chlorides	3
061789-86-4	Petroleum sulfonic acids, calcium salts	3
061789-91-1	Jojoba bean oil	3
061789-99-9	Lard	4A
061790-12-3	Fatty acids, tall-oil	3
061790-31-6	Amides, tallow, hydrogenated	3
061790-33-8	Amines, tallow alkyl	3
061790-38-3	Fatty acids, tallow, hydrogenated	4B
061790-47-4	Amines, rosin alkyl	3
061790-51-0	Rosin acids, sodium salt	3
061790-53-2	Diatomaceous earth (less than 1% crystalline silica)	4A
061790-66-7	Fatty acids, tall oil, compounds with diethanolamine	3
061790-81-6	Ethoxylated lanolin	3
061790-85-0	Ethoxylated N-(tallow alkyl)trimethylene diamines	3
061790-86-1	Fatty acids, tall-oil, monoesters with sorbitan, ethoxylated	3
061790-88-3	Sorbitan, tall-oil fatty acids triesters, ethoxylated	3
061790-93-0	Fatty acids, tall-oil, tetraesters with sorbitol, ethoxylated	4B
061791-00-2	Fatty acids, tall-oil, ethoxylated	3
061791-06-8	Polyethylene glycol sesquiester of tallow acids	3
061791-12-6	Castor oil, ethoxylated	4B
061791-14-8	Amines, coco alkyl, ethoxylated	3
061791-24-0	Amines, soya alkyl, ethoxylated*	3
061791-26-2	Amines, tallow alkyl, ethoxylated	4B
061791-28-4	Alcohols, tallow, ethoxylated	3
061791-31-9	N,N-Bis(2-hydroxyethyl)(coconut oil alkyl)amine	4B
061791-38-6	1H-Imidazole-1-ethanol, 4,5-dihydro-, 2-norcoco alkyl derivatives	3
061791-41-1	N-Methyl-N-(tall-oil acyl)taurine, sodium salt	3
061791-55-7	N-Tallow alkyltrimethylenediamines	3
061791-63-7	Amines, N-coco alkyltrimethylenedi-	3
061849-72-7	Polypropylene glycol beta-methyl glucoside ether (4:1)	3
063148-62-9	Silicones and siloxanes, dimethyl	4B
063148-69-6	Alkyd resins (alcohols, polyhydric, polyesters)	3
063231-60-7	Paraffin waxes and hydrocarbon waxes, microcryst	3
063231-67-4	Silica gel	4A
063415-74-7	Poly[oxy(methyl-1,2-ethanediyl)], alpha-butyl- omega -(2-propenyloxy)-	3
063449-39-8	Chlorinated wax	3

U.S. Environmental Protection Agency
Office of Pesticide Programs
List of Inert Pesticide Ingredients
List 3 - Inerts of unknown toxicity - By CAS Number
Updated August 2004

		propanediamine salt	
60816-63-9		Ethylenediaminetetraacetic acid, triethylamine salt	3
60828-92-4		Isopropylamine sulfate	3
60840-87-1		Sodium N-oleoyl taurine	3
60874-90-0		Sodium isopropyl isobutyl naphthalenesulfonate	3
60883-84-3		Methylnonylnaphthalenesulfonic acid, sodium salt	3
60883-89-8		Tridecylbenzenesulfonic acid, dimethylamine salt	3
60883-90-1		Tridecylbenzenesulfonic acid, propylamine salt	3
60933-42-8		Trimethylnaphthalenesulfonic acid, sodium salt	3
61181-29-1		Lauryl methacrylate, copolymer with ethylene glycol dimethacrylate	3
61524-98-9		Ethoxylated hydroabiethyl alcohol	3
61702-73-6	1H-	Imidazolium, 1,1-bis(carboxymethyl)-4,5-dihydro-2-undecyl-, hydroxide, disodium salt	3
61757-59-3		Poly(oxyethylene)tridecylacetate, sodium salt	3
61788-44-1		Phenol, styrenated	3
61788-47-4		Coconut oil fatty acids	3
61788-48-5		Acetylated lanolin	3
61788-59-8		Fatty acids, coco, Me esters	3
61788-72-5		Epoxidized octyl tallate	3
61788-85-0		Castor oil, hydrogenated, ethoxylated	3
61788-89-4		Fatty acids, C18-unsatd., dimers	3
61788-90-7		Coco alkyldimethylamines, N-oxides	3
61788-93-0		Coco alkyldimethylamines	3
61789-01-3		Tall oil, epoxidized, 2-ethylhexyl esters	3
61789-18-2		Coco alkyltrimethyl quaternary ammonium chlorides	3
61789-31-9		Soap, coconut oil	3
61789-36-4		Calcium naphthenate	3
61789-40-0	N-(	Coco alkyl) amido propyl dimethyl betaine	3
61789-51-3		Cobalt naphthenate	3
61789-60-4		Pitch	3
61789-65-9		Resin acids and rosin acids, aluminum salts	3
61789-72-8		Dimethyl benzyl hydrogenated tallow ammonium chloride	3
61789-73-9		Quaternary ammonium compounds, benzylbis(hydrogenated tallow alkyl)methyl, chlorides	3
61789-75-1		Benzyl dimethyl (tallow alkyl) ammonium chloride	3
61789-76-2		Dicoco alkylamine	3
61789-77-3		Quaternary ammonium compounds, di(coco alkyl)dimethyl, chlorides	3
61789-81-9		Quaternary ammonium compounds, bis(hydrogenated tallow alkyl)dimethyl, Me sulfates	3
61789-86-4		Petroleum sulfonic acids, calcium salts	3
61789-91-1		Jojoba bean oil	3
→ 61790-12-3		Fatty acids, tall-oil	3
61790-50-9		Potassium salt of wood rosin acids	3

PAN Pesticides Database - Pesticide Registration Status

Home > Country Registration

Help | Feedback

Regulatory Information for Tall oil use in United States

Registered for Use:	Yes
Banned or Restricted:	
Consent to Import:	
Notes:	This chemical is listed as 'Registered' because there are U.S. registered products that contain this chemical or it is specifically registered for use in California.
Source:	PAN Compiled List of US Registered Active Ingredients, Pesticide Action Network North America, February 12, 2005 From Pesticide Product Information System, U.S. EPA, June 26, 2006, and California Registered active ingredients, California Department of Pesticide Regulation, January 28, 2005. See documentation for full explanation of methodology used to create the US Registered list.

Related Chemicals for Tall oil

Top

Note! See related chemicals for additional registration information. Different forms of a chemical may be regulated differently.

CAS Number	Relation	Reason	Chemical Name	Chem Detail	Registration	Symptoms	California Use	Chem Use Type	U.S. EPA Reg	PAN Bad Actor
8002-26-4	Parent	P	Tall oil	View	View	View	View	Adjuvant	Yes	Not Listed
	Related	11	Fatty acids derived from tallow	View	View	View	View	Adjuvant	Yes	Not Listed
61790-12-3	Related	11	Tall oil acids	View	View	View	View	Adjuvant	Yes	Not Listed

Citation: Kegley, S.E., Hill, B.R., Orme S., Choi A.H., *PAN Pesticide Database*, Pesticide Action Network, North America (San Francisco, CA, 2008), http:www.pesticideinfo.org

Section 8 List of Attachments

Attachment 1, section 8: High Production Information System (HPVIS): about reference Final Submission Information for Tall Oil and Related Substances Zinkel, D.F. and Russell, J., Eds. 1989. Naval Stores Production, Chemistry, Utilization. Pulp Chemicals Association, New York.).

Attachment 2, section 8: Label of Timorex Gold

Attachment 3, section 8: Pine Chemical Association, Atlanta: High Production Volume Chemical Challenge Program, Test Plan for Tall Oil and Related Substances, Submitted to US EPA

Attachment 1, Section 8

Use Information

Category Chemical:	(8002-26-4) Tall oil
Test Substance:	(8002-26-4) Tall oil
Test Substance Purity/Composition and Other Test Substance Comments:	All of the substances in this category are derived from or closely related to tall oil, a by-product from the pulping of pine trees. Tall oil and the various derivatives in this category are complex mixtures and therefore considered to be Class 2 substances. They are composed of numerous chemicals, the most common of which are rosin and fatty acids, with lesser amounts of terpenes and sterols. However, all the members of this category are similar in chemical composition, being predominantly the extractives that remain after the pulping of wood. This description of Use Information applies to all of the substances in this category.
Reference:	Final Submission for Tall Oil and Related Substances Zinkel, D.F. and Russell, J., Eds. 1989. Naval Stores. Production, Chemistry, Utilization. Pulp Chemicals Association, New York.
Description:	
Use Pattern:	Human exposure is limited by the fact that most tall oil chemicals are industrial intermediates consumed in the production of other chemicals. Approximately 95% of tall oil is consumed during the production of other downstream products. Consequently, there is little, if any potential for exposure of the general consumer population. Environmental exposure is limited by the fact that the chemical processes used in the tall oil industry are essentially closed system processes where temperature and pressure are carefully controlled. Tall oil is by far the most important member of this category from a commercial standpoint. The main use of tall oil is as a feedstock to the fractionation process, where it is separated into its various fractions (rosin, fatty acids, distilled tall oil, heads, pitch). Tall oil pitch, a tarry substance, is mainly consumed as fuel by the tall oil processor. Tall oil pitch, sodium salt is used in the asphalt industry as a bonding agent in paving applications, or as a plasticizer in asphalt coatings. Tall oil, disproportionated is important in the copolymerization of styrene and butadiene to produce rubber (SBR) and it is also used in the production of neoprene. Tall oil, disproportionated, potassium salt is used in the rubber industry as an emulsifying agent. Tall oil, sodium and potassium salts are used in the production of soaps and detergents, as well as in metalworking fluids and lubricants. Tall oil soap acidulation wastewater is composed of dilute tall oil and is of no commercial value. It is either recycled to the pulping process for the relatively small sodium value or is routed to the producer's wastewater treatment system. Table 1 illustrates general use categories of tall oil and the other substances in this category.

A Hachment 2, section 8

TIMOREX *Gold* EC

Directions for use ● *Carefully read the lable befor use*

Safety Precautions The compound should be handled with care and used according to the accepted safety rules for usage of biocides. It is recommended to use safety glasses. Do not swallow or inhale. Do not spray directly on skin or eyes.

Preparation of the spray Fill half of sprayer with water, add the compound in the right concentration while stirring and fill-up with the remaining water.

Shake well before use* ● *Do not spray during the warm hours

Batch No. .... Content: .... liter
UN number - unclassified ● Hazard Level 3
Flora Protection License number 7266/PPIS/05

TIMOREX dloG has been tested on a limited range of plant species for phytotoxic effects. Some plant species are more sensitive than others. For further details on plant safety contact the manufacturer.

Manufacturer and license-holder
BIOMOR ISRAEL Ltd. www.biomor.com ● biomor@biomor.com
Distributed by Stockton Chemical Corp.
16 Menachem Begin St. Gama House, Ramat Gan 52521, Israel
● Tel. 972-3-6130770 ● Fax. 972-3-6130771

Natural BioFungicide

TIMOREX *Gold* EC

For the control of foliar diseases in vegetables, herbs and grapevines, in open fields and green houses.

Contains 24% *Melaleuca alternifolia* oil

Crop	Disease	Concentration/Dose	Apply Every 7-10 days
Qucorbit	Powdery Mildew Downy Mildew	0.4%-0.7% *	in 200-800 liters water /ha
Pepper	Powdery Mildew	0.4%-0.7% *	in 200-800 liters water /ha
Tomato	Powdery Mildew	0.4%-0.7% *	in 200-800 liters water / ha
Grapevine	Powdery Mildew Downy Mildew	0.4%-0.7% *	in 600-1500 liters water /ha
Herbs	Powdery Mildews Gray Mold (Botrytis)	0.4%-0.7% *	in 200-400 liters water /ha

Approved for Use in Organic Agriculture

* When disease has appeared use the higher concentration.
‣ As For prophylactic treatment use 0.5%.
‣ Pre Harvest Interval 3 days.

BIOMOR

TIMOREX *Gold* EC

After treatment

Cleaning of sprayer and immersion container After spraying, clean sprayer and/or container with water. Make sure that remnants of material do not infect cultivated fields and water sources.

With time, the material might damage plastic parts; consequently, it is important to clean the container well.

Storage **TIMOREX** *Gold* contains volatile materials. Store in original container, tightly closed and in a dry, cool place.

Store the compound in a locked place, especially assigned for storage of pesticides, out of the reach of children and untrained adults. Keep compound away from human or animal food.

Handling of empty containers Empty containers have to be brought to a poisonous materials site, especially for pesticides and approved by the Ministry of Environment.

Handling of spilled materials Absorb with sand or sawdust and clean the place thoroughly with soap and water. If compound is leaking, has expired, or has been spoiled during storage, it has to be taken to a materials site, especially for compound and approved by the Ministry of Environment.

First Aid In case of contact with the skin, rinse the area thoroughly with soap and water. In case of contact with eyes, rinse thoroughly in running water for 15 minutes and immediately see a doctor, bringing the label. After spraying, thoroughly wash hands and all other body-parts, which have been in contact with the compound.

Produced by BIOMOR Ltd.

The user is responsible for all damage, caused by factors outside the control of the manufacturer. The manufacturer is not responsible for any damage caused by incorrect storage or handling, not according to the explicit directions on the organic biocide label.

~~Attached~~ Attachment 3, section 8.

page 1

AR 201 - 13055

PINE CHEMICALS ASSOCIATION

P.O. BOX 105113 • ATLANTA, GA 30348-5113 • (770) 446-1290 • FAX (770) 446-1487

May 23, 2001

DEC 15 2008

Administrator
US EPA
P.O. Box 1473
Merrifield, VA 22116

Re: HPV Test Plans and Robust Summaries for Tall Oil and Related Substances and Tall Oil Fatty Acids and Related Substances

Dear Ms Whitman;

On behalf of the member companies of the Pine Chemicals Association's High Production Volume Chemical Task Force, I am pleased to submit the Test Plans and Robust Summaries for the chemical categories designated as:

"Tall Oil and Related Substances"

"Tall Oil Fatty Acids and Related Substances"

The submission includes one electronic copy of each in pdf format, and a hard copy which will be mailed to EPA Headquarters. The registration number for our Consortium is

Should you have any questions concerning our submission please feel free to contact me at (770) 209-7534 or at wjones@tappi.org.

Sincerely,

Walter L. Jones
President & COO

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MR 48236

attachment 3, section 8
page 2

AR201-13056A

HIGH PRODUCTION VOLUME (HPV)
CHEMICAL CHALLENGE PROGRAM

TEST PLAN

for

TALL OIL
AND
RELATED SUBSTANCES

CAS No. 8002-26-4
CAS No. 8016-81-7
CAS No. 68140-16-9
CAS No. 68152-92-1
CAS No. 65997-01-5
CAS No. 68647-71-2
CAS No. 65997-02-6

Submitted to the US EPA

BY

The Pine Chemicals Association, Inc.
HPV Task Force
Consortium Registration #

Table of Contents

Test Plan For Tall Oil and Related Substances

Test Plan for Tall Oil and Related Substances

Summary

The Pine Chemicals Association, Inc. (PCA) is sponsoring 36 HPV chemicals. This Test Plan addresses the following seven chemicals, known collectively as Tall Oil and Related Substances:

8002-26-4, Tall Oil
8016-81-7, Tall Oil Pitch
68140-16-9, Tall Oil Pitch, sodium salt
68152-92-1, Tall Oil, disproportionated
65997-01-5, Tall Oil, sodium salt
68647-71-2, Tall Oil, potassium salt
65997-02-6, Wastewater, tall oil soap acidulation

These seven substances are all derived from or closely related to tall oil, a by-product from the pulping of pine trees. Tall oil and the various derivatives in this group are all complex mixtures (Class 2 substances). They are composed of numerous chemicals -- the most common of which are rosin and fatty acids, with lesser amounts of terpenes and sterols. Each species of pine tree yields a somewhat different mix of tall oil, and even within a species, the composition of the tall oil could be influenced by the climate and local terrain. However, all the members of this group are similar in chemical composition, being predominantly the extractives that remain after the pulping of wood. Thus, PCA has elected to treat these chemicals as a category for purposes of the HPV program.

Where applicable, PCA will conduct physical/chemical property and environmental fate testing on these substances. Available data show tall oil is non-toxic in acute studies. PCA will conduct testing for the other SIDS health effects endpoints. A representative of the category will be used for ecotoxicity, *in vitro* genotoxicity, and mammalian toxicity testing.

Tall oil is the source of most of the substances in this category, except acidulation wastewater (which is essentially wastewater containing about 1 - 2 % tall oil). Tall oil is used as the feedstock for fractional distillation, from which a variety of useful fractions (rosin, fatty acids, distilled tall oil, heads and pitch) are derived.

Tall oil pitch (the residue after other fractions are distilled away) is primarily consumed as fuel by the tall oil processor; small amounts are converted to salts for use in the asphalt industry. Tall oil salts are used in the production of soaps and detergents, and in metal working fluids. Disproportionated tall oil is used in the rubber industry as a processing aid.

Tall oil (CAS# 8002-26-4) has been selected as the representative substance in this group for testing for the SIDS data. PCA has reviewed existing data on tall oil and determined that other than acute toxicity, there are no other data on the SIDS endpoints. The available data demonstrate that tall oil is non-toxic following acute oral exposure. Because there are no data on ecotoxicity, repeat dose toxicity, *in vitro* genotoxicity, reproductive or developmental toxicity, tall oil will be tested to fulfill these endpoints. A brief summary of the available data for the substances in this category, and the anticipated additional testing, is described below and in Table 1.

Table 1
Matrix of Available Adequate Data and Proposed Testing On Tall Oil and Related Substances*

Chemical and CAS #	Required SIDS Endpoints										
	Partition Coef.	**Water Sol.**	**Biodeg.**	**Acute Fish**	**Acute Daph.**	**Acute Algae**	**Acute oral**	**Repeat Dose**	**In vitro genetox (bact.)**	**In vitro genetox (non-bact)**	Repro/ Develop
8002-26-4, Tall Oil	Test	Test	Adeq.	Test	Test	Test	Adeq.	Test	Test	Test	Test/ Test
8016-81-7, Tall Oil Pitch	Test	LM	Adeq.	C	C	C	C	C	C	C	C
68140-16-9, Tall Oil Pitch, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C
68152-92-1, Tall Oil, disproportionated	Test	Test	Test	C	C	C	C	C	C	C	C
65997-01-5, Tall Oil, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C
68647-71-2, Tall Oil, potassium salt	Test	Test	Test	C	C	C	C	C	C	C	C
65997-02-6, Wastewater, tall oil soap acidulation	No test	No test	No test	C	C	C	C	C	C	C	C

Adeq. Indicates adequate existing data
Test Indicates proposed testing
No test See test plan for explanation
LM Lack of a suitable analytical method precludes testing
C Indicates category read-down from existing or proposed test data on tall oil.
*No testing will be conducted for melting point, boiling point, vapor pressure, hydrolysis, photodegradation and transport and distribution between environmental compartments, as explained in the test plan.

Physical/Chemical Properties

Physical and chemical properties will be determined when appropriate; however, many of the physical and chemical properties are either inappropriate or cannot be measured for these compounds:

- The melting point will not be determined because these substances will not give a sharp melting point.
- Boiling points cannot be determined because these substances will decompose before they boil.
- Under ambient conditions, the vapor pressure of these chemicals is essentially zero and experimental measurement is not possible.
- The partition coefficients will be tested for six of the substances in this category. Partition coefficient testing can yield a range of values representing the various components, rather than a single value representing the mixture.
- The water solubility of five of the compounds in this grouping category will be determined.

Environmental Fate

With respect to the SIDS environmental fate endpoints:

- Determination of photodegradation is not relevant, since the vapor pressure of these compounds at ambient temperature is essentially zero and they could not enter the atmosphere.
- Hydrolysis in water will not be determined for any of the compounds in this category because the members of this category have low water solubility and lack a functional group that would be susceptible to hydrolysis.
- Biodegradation data will be generated for four of the compounds for which data are not already available.
- Transport and distribution between environmental compartments will not be determined due to the inability to provide usable inputs to the required model.

Ecotoxicity

- Existing **ecotoxicity** data are not reliable due to inconsistencies in, or artificial methods of, sample preparation. Consequently, tall oil will be retested for acute toxicity to fish, daphnia and algae under conditions that maximize the solubility, but reduce exposure to insoluble fractions that may cause nonspecific toxicological effects.

Mammalian Toxicity

- For the SIDS human health endpoints, there are sufficient data on acute toxicity for tall oil demonstrating that this compound is non-toxic. Data will be generated for tall oil for repeat dose toxicity, reproductive and developmental toxicity using OECD 422, as well as ***in vitro*** genotoxicity testing.

The Pine Chemicals Association, Inc. HPV Task Force includes the following companies:

Akzo Nobel Resins
Akzo Nobel - Eka Chemicals Incorporated
Arizona Chemical Company
Asphalt Emulsion Manufacturers Association
Boise Cascade Corporation
Cognis Corporation
Eastman Chemical Co. (including the former Hercules Inc. Resins Division)
Georgia-Pacific Resins Inc.
ICI Americas (including the former Uniqema)
Inland Paperboard & Packaging, Inc.
International Paper Co. (including the former Champion International Corporation)
Koch Materials Co.
McConnaughay Technologies, Inc.
Mead Corp.
Packaging Corporation of America
Plasmine Technology, Inc.
Raisio Chemicals
Rayonier
Riverwood International
Smurfit - Stone Container Corporation
Westvaco
Weyerhaeuser Co.

The Task Force will be filing multiple test plans covering various chemicals. Not all members of the Task Force produce the substances covered by this test plan.

I. Description of Tall Oil and Related Substances

The Pine Chemicals Association, Inc. (PCA) is sponsoring seven HPV chemicals known collectively as Tall Oil and Related Substances. This group of chemicals consists of the following:

8002-26-4, Tall Oil
8016-81-7, Tall Oil Pitch
68140-l 6-9, Tall Oil Pitch, sodium salt
68152-92-1, Tall Oil, disproportionated
65997-01-5, Tall Oil, sodium salt
68647-71-2, Tall Oil, potassium salt
65997-02-6, Wastewater, tall oil soap acidulation

This group of chemicals are all closely related to tall oil, which is a by-product from the alkaline pulping of wood, especially pinewood. The precursors of tall oil in the tree are the so-called extractives that make up about 1% of the weight of the wood. These extractives are composed of numerous chemicals, the most common of which are rosin and fatty acids, with lesser amounts of terpenes and sterols. The extractives dissolve in the pulping liquor and are recovered from the liquor when it is concentrated and skimmed. The skimmed material is called tall oil soap and is the sodium salt of tall oil (CAS# 65997-01-5).

Tall oil soap is then acidulated with sulfuric acid to yield crude tall oil (CAS# 8002-26-4). A by-product of this acidulation is “wastewater, tall oil soap acidulation” (CAS# 65997-02-6), which is essentially a solution of sodium sulfate containing dilute amounts of tall oil. Commercially, crude tall oil is fractionally distilled to manufacture tall oil fatty acids and tall oil rosin. These important substances are the key members in other categories of HPV chemicals being sponsored by the Pine Chemicals Association, Inc. An intermediate fraction from the distillation process is distilled tall oil, which has the same CAS registry number as crude tall oil.

The other members of this HPV category are all closely related to tall oil. Disproportionated tall oil (CAS# 68152-92-1) is tall oil that has been stabilized to oxidation. Tall oil pitch (CAS# 8016-81-7) is the residue remaining when the tall oil fatty acids and the tall oil rosin have been distilled away. Its main use is for its fuel value. Zinkel and Russell (1989) noted that use of a material similar to tall oil pitch dates back to biblical times. In Genesis 6:14, Noah was instructed to *"pitch the ark within and without,"* indicating the historical use of pine tree resins, The remaining members of the group are simple salts of either tall oil or pitch.

As complex mixtures, tall oil and its derivatives are all considered Class 2 substances. Information on their composition, uses and the challenges of chemical analysis of these complex mixtures is described below.

A. Composition

All the members of this category are chemically complex, with their composition dependent on the source of the trees from which they were derived and the conditions under which the tall oil was distilled. They are all Class 2 substances. Consequently, they are not described in terms of their chemical composition, but only in general terms such as their acid number or their overall fatty acid or resin acid content (Zinkel and Russell 1989). However, some general information on the typical composition of each of the seven substances in this category is provided below.

1. Tall Oil (CAS# 8002-26-4)

The TSCA Inventory describes tall oil as, "*A complex combination of tall oil rosin and fatty acids derived from acidulation of crude tall oil soap and including that which is further refined. Contains at least 70% rosin.* " The two chief types of tall oil covered by this description are crude tall oil and distilled tall oil. The composition of a typical crude tall oil produced in the southeastern U.S. and a typical distilled tall oil are given in Table 2.

Table 2

Composition of Typical Tall Oils

	Crude Tall Oil	**Distilled Tall Oil**
Acid number	165	185
Fatty acids (%)	52	65
Resin acids (%)	40	30
Unsaponifiable matter (%)	8	5

The actual composition of both types of tall oil can vary widely. The composition of crude tall oil depends on the species of tree from which it was derived, while the composition of distilled tall oil depends upon the species of tree as well as the processing conditions under which it was manufactured. More detailed information on the composition of the tall oil to be tested for the HPV endpoints is provided in Table 3. The structures of some representative resin acids are shown in Figure 1.

Table 3
Comoosition of Distilled Tall Oil To Be Tested

Palmitic acid	$CH_3(CH_2)_{14}COOH$	3%
Palmitoleic acid[a]	$CH_3(CH_2)_XCH=CH(CH_2)_YCOOH$	1%
Stearic acid	$CH_3(CH_2)_{16}COOH$	1%
Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	28%
Linoleic acid	$CH_3(CH_2)_4CH=CH\text{-}CH_2CH=CH(CH_2)_7COOH$	19%
Linoleic acid, conjugated[b]	$CH_3(CH_2)_XCH=CHCH=CH\text{-}(CH_2)_YCOOH$	9%
Other fatty acids[c]		7%
Isopimaric acid		3%
Abietic acid		10%
Dehydroabietic acid		5%
Other resin acids		11%

---

a: $x+y=12$

b: x usually 4 or 5; y usually 7 or 8; but $x + y = 12$

c: 5,9,12-octadecatrienoic acid; linolenic acid; 5,11,14-eicosatrenoic acid; cis,cis-5,9-octadecadienoic acid; eicosadienoic acid: elaidic acid; cis-1 1 octadecanoic acid; C-20, C-22, C-24 saturated acids.

2. Tall Oil Pitch (CAS# 8016- 81-7)

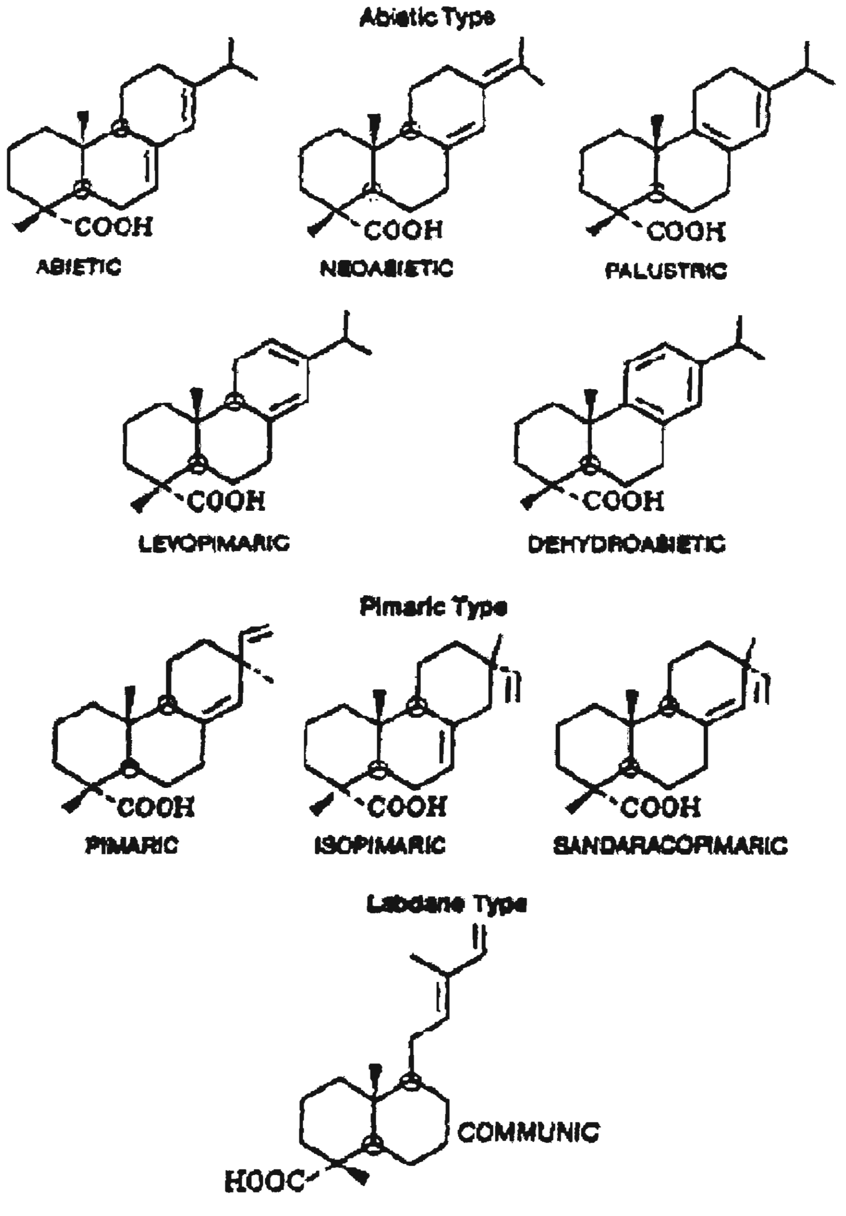
Tall oil pitch is a tarry semi-solid material with a composition very dependent on the processing conditions under which it was produced. As a consequence of its low acid number, its complex composition and its physical form, most of the pitch produced is consumed for its fuel value.

The TSCA Inventory defines tall oil pitch as ***"the residue from the distillation of tall oil. It contains primarily high boiling esters of fatty acids and rosin. It may also contain neutral materials, free fatty acids and resin acids".*** Pitch is primarily made up of high boiling, high molecular weight compounds formed at the high temperatures encountered during the fractionation process. These compounds include the esters of fatty acids and rosin, and small amounts of dimers and trimers of resin acids and fatty acids. Because pitch has such an extremely complex and variable composition, chemical analysis is not possible, and no typical composition can be presented.

3. Tall Oil Pitch, Sodium Salt (CAS# 68140- 16-9)

This substance is made by neutralizing tall oil pitch with sodium hydroxide. It is sold as an aqueous dispersion.

Figure 1



Common Resin Acids

Figure 1 shows the structures of some representative resin acids found in distilled tall oil and its derivatives.

4. Tall Oil, Disproportionated (CAS# 68152-92-l)

Disproportionated tall oil is distilled tall oil that has been heated with a catalyst that removes conjugated double bonds. The fatty acid and resin acid contents of the treated product are the same as the starting distilled tall oil (see Table 2), but some of the individual components are changed. For example, abietic acid is converted to dehydroabietic acid and linoleic acid is converted to oleic acid.

5. Tall Oil, Sodium Salt (CAS # 65997-01-5) and Potassium Salt (CAS # 68647-71-2)

The sodium salt of crude tall oil is also known as tall oil soap, the precursor to tall oil. Both the sodium and potassium salts of tall oil are also produced from distilled tall oil. The salts are made by treating tall oil with the appropriate base and dispersing the salt formed in water. These compounds, as the salts of a strong base and a weak acid, result in alkaline dispersions with the pH dependent on the salt concentration in the dispersion.

6. Wastewater, Tall Oil Soap Acidulation (CAS # 65997-02-6)

The TSCA Inventory defines this byproduct as, *"The aqueous layer formed by acidulation of tall oil soap with sulfuric acid during the production of tall oil. Composed primarily of a solution of sodium sulfate, the remainder being lignin and tall oil.* " Typically, tall oil soap acidulation wastewater is about a 12% solution of sodium sulfate, containing about 1 to 2% tall oil. This material has no commercial value except as a minor source of sodium for a kraft pulp mill. When that outlet is not available, the wastewater is typically discharged into a mill's wastewater treatment system.

No testing is planned for this material. The Pine Chemicals Association, Inc. (PCA) and the American Forest & Paper Association (AF&PA) petitioned the EPA to remove this byproduct from the HPV list on the grounds that it is an inorganic byproduct and should not be on the list, EPA suggested instead that this material should be treated as "dilute tall oil" since it contains some minor amount of tall oil and did not require independent testing.

B. Commercial Uses of Tall Oil and Related Substances

Tall oil is by far the most important member of this category from a commercial standpoint. The main use of tall oil is as a feedstock to the fractionation process, where tall oil is separated into its various fractions (rosin, fatty acids, distilled tall oil, heads, pitch).

Tall oil pitch, a tarry substance, is mainly consumed as fuel by the tall oil processor.

Tall oil pitch, sodium salt is used in the asphalt industry as a bonding agent in paving applications, or as a plasticizer in asphalt coatings.

Tall oil, disproportionated is important in the copolymerization of styrene and butadiene to produce rubber (SBR) and it is also used in the production of neoprene.

Tall oil, sodium and potassium salts are used in the production of soaps and detergents, as well as in metalworking fluids and lubricants.

Tall oil soap acidulation wastewater is composed of dilute tall oil and is of no commercial value. It is either recycled to the pulping process for the relatively small sodium value or is routed to the producer's wastewater treatment system.

C. Complexity of Analytical Methodology

All of the substances in this category are Class 2 substances. This, combined with the fact that tall oil is essentially insoluble in water and decomposes on heating at high temperature, creates a variety of analytical issues. Gas chromatography of methylated derivatives is the accepted method for the analysis of the members of this category. However, the solubility of tall oil is very low (about 10 ppm). PCA has verified the reliability of the standard analytical methods at such low concentrations. Based on the method validation work to date, it appears that the analytical procedures for tall oil and the remaining substances in this group (with the exception of pitch) will be adequate for the proposed testing. In spite of intensive efforts to develop an analytical method for pitch, analysis has proved to be impossible due to the complexity of this material.

II. Rationale for Selection of Representative Compound for Testing

Tall oil (CAS# 8002-26-4) (which includes crude and distilled tall oil) has been chosen as the representative of this category for testing purposes because it is commercially the most important member of the category. It is the commercial source of most of the substances in this category and the others are associated with its production. In addition, tall oil is the source of almost all of the 36 substances included in the entire PCA HPV program.

All the substances in this category are similar in chemical composition, being predominantly tall oil or its salts. Distilled tall oil will be used as the representative substance in this group for testing for the applicable SIDS ecotoxicity and mammalian toxicity tests. Distilled tall oil is more uniform in composition and physical state than crude tall oil. In addition, products based on distilled tall oil are far more common than those based on crude tall oil, which is used almost exclusively as a distillation feed.

Another criterion listed by EPA for grouping chemicals into a category is the use of the "family approach" of examining related chemicals when they are acids or acid salts, Although the salts of tall oil and tall oil pitch have different physical characteristics, they are included in this group because they are quickly converted into the free tall oil or tall oil pitch when they are treated by acid or by dilution, as they would be under typical toxicity testing conditions.

In summary, this category of chemicals fits the requirements of the EPA's HPV Challenge program for a chemical category, and tall oil is the most appropriate representative test material from this category.

III. Review of Existing Data and Development of Test Plan

PCA has undertaken a comprehensive evaluation of all relevant data on the SIDS endpoints of concern for the chemicals in this category. Other than acute toxicity, there are no other data on the HPV SIDS endpoints for this category. The availability of the data on the specific SIDS endpoints is summarized in Table 4 (identical to Table 1). Table 4 also shows where data will be generated.

Table 4
Matrix of Available Adequate Data and Proposed Testing
On Tall Oil and Related Substances*

Chemical and CAS #	Required SIDS Endpoints										
	Partition Coef.	Water Sol.	Biodeg.	Acute Fish	Acute Daph.	Acute Algae	Acute oral	Repeat Dose	In vitro genetox (bact.)	In vitro genetox (non-bact)	Repro/ develop
8002-26-4, Tall Oil	Test	Test	Adeq.	Test	Test	Test	Adeq.	Test	Test	Test	Test/ Test
8016-81-7, Tall Oil Pitch	Test	LM	Adeq.	C	C	C	C	C	C	C	C
68140-16-9, Tall Oil Pitch, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C
68152-92-1, Tall Oil, dispro-portionated	Test	Test	Test	C	C	C	C	C	C	C	C
65997-01-5, Tall Oil, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C
68647-71-2, Tall Oil, potassium salt	Test	Test	Test	C	C	C	C	C	C	C	C
65997-02-6, Wastewater, tall oil soap acidulation	No test	No test	No test	C	C	C	C	C	C	C	C

Adeq. Indicates adequate existing data
Test Indicates proposed testing
No **test** See test plan for explanation
LM Lack of a suitable analytical method precludes testing
C Indicates category read-down from existing or proposed test data on tall oil.

*No testing will be conducted for melting point, boiling point, vapor pressure, hydrolysis, photodegradation, and transport and distribution between environmental compartments as explained in the test plan.

A. Evaluation of Existing Physicochemical Data and Proposed Testing

The basic physicochemical data required in the SIDS battery includes melting point, boiling point, vapor pressure, partition coefficient (K_{ow}), and water solubility.

Class 2 substances are composed of a complex mixture of substances and are often difficult to characterize. As noted above, tall oil, tall oil pitch, disproportionated tall oil and their various salts are Class 2 substances. Their composition is variable and cannot be represented by a definite chemical structural diagram. Due to this "complex mixture" characteristic of tall oil and related compounds, some physical property measurements, such as the partition coefficient are of questionable value because the methodology used to determine these properties will actually fractionate or partition the substances into various components. Since the methodology will alter the actual sample composition, the results of these tests are likely to be erroneous, difficult to interpret or meaningless.

1. Melting Point

Tall oil and the other non-salts in this grouping category are liquids at room temperature; tall oil pitch is a semi-solid. A sharp melting point cannot be obtained for any of these compounds due to the complex nature of these substances. The salts are solids under ambient conditions and heating them to determine the melting point would cause thermal decomposition.

2. Boiling Point

All of the non-salt members of this category are produced by high temperature, high vacuum distillation and are non-volatile at ambient temperatures. A boiling point at ambient pressure has no significance because when heated to high temperatures these materials will thermally decompose before they boil. The two salts in this category are solids. When heated to high temperatures, they will also thermally decompose before boiling. Accordingly, measurement of this property is inappropriate for all the substances in this category.

3. Vapor Pressure

Vapor pressures for tall oil and the other chemicals in this category at ambient temperatures are effectively zero, and their experimental measurement is inappropriate. The salt members of the category are solids and thus have no vapor pressure, so this end point cannot be measured. When dissolved in water, their solutions will reflect the vapor pressure of the water rather than the salt, and therefore measurement of this property is inappropriate.

4. Water Solubility

The water solubility of five compounds in this category will be determined using OECD protocol (105). The lack of a suitable analytical method for tall oil pitch precludes the determination of the water solubility.

5. Partition Coefficient

The partition coefficient (i.e., K,,) for six compounds in this category will be determined. Adequate data exist for tall oil and pitch although both will be retested with the other compounds in this category. Because all of these substances are Class 2 mixtures, the procedure (OECD 107) to determine the K_{ow} often yields a number of separate K_{ow} values rather than a single value representative of the mixture. Thus, the results will represent the partition coefficients of the components rather than the mixture.

Summary of Physicochemical Properties Testing: The water solubility of tall oil, disproportionated tall oil and two of the salts will be determined. The partition coefficients for six members of this category will be determined. Adequate data exist for tall oil and pitch although both will be retested with the other compounds in this category. Tests for the melting point, boiling point and vapor pressure are inappropriate.

B. Evaluation of Existing Environmental Fate Data and Proposed Testing

The fate or behavior of a chemical in the environment is determined by the rates or half-lives for the most important transformation (degradation) processes. The basic environmental fate data covered by the HPV Program includes biodegradation, stability in water (hydrolysis as a function of pH), photodegradation and transport and distribution between environmental compartments.

1. Biodegradation

Biodegradability provides a measure for the potential of compounds to be degraded by microorganisms. Depending on the nature of the test material, several standard test methods are available to assess potential biodegradability.

Of the chemicals in this category, two (tall oil and tall oil pitch) have existing data on the biodegradation endpoint. Biodegradation for disproportionated tall oil and the three salts will be determined.

2. Hydrolysis

Hydrolysis as a function of pH is used to assess the stability of a substance in water. Hydrolysis is a reaction in which a water molecule (or hydroxide ion) substitutes for another atom or group of atoms present in an organic molecule. If there is no group suitable to be displaced, then the organic compound is considered to be resistant to hydrolysis. None of the substances in the tall oil category contains an organic functional group that might be susceptible to this physical degradative mechanism. Therefore, hydrolysis need not be measured.

In addition, low water solubility often limits the ability to determine hydrolysis as a function of pH. All of the tall oil compounds have very low solubility in water. Therefore, these materials are expected to be stable in water and it would be unnecessary to attempt to measure the products of hydrolysis. With respect to the various tall oil salts, since they exist in an aqueous medium they hydrolyze (ionize) immediately, but form stable species. Consequently, it would also be unnecessary to measure this endpoint for tall oil salts.

3. Photodegradation

Due to their low water solubility and lack of any vapor pressure at ambient temperatures, there is no opportunity for any of these chemicals to enter the atmosphere. Thus, photodegradation is irrelevant. In addition, based on the constituents in these.complex mixtures, there is no reason to suspect that they would be subject to breakdown by a photodegradative mechanism. Consequently, this endpoint will not be determined for any of the substances in this category.

4. Transport and Distribution Between Environmental Compartments

The transport and distribution between environmental compartments is intended to determine the ability of a chemical to move or partition in the environment. The determination of this property requires the use of various models (e.g., level III model from the Canadian Environment Modeling Centre at Trent University). For Class 2 substances such as tall oil and related compounds, the required inputs to the model are either not available or impossible to determine including molecular mass, reaction half-life estimates for air, water, soil, sediment, aerosols, suspended sediment, and aquatic biota. In addition, while the partition coefficient is also required and can be determined, the multiple K_{ow} values typically derived for these substances (e.g., eight K_{ow} values for tall oil) are a consequence of sample fractionation and reflect various components in the mixture and are not representative of the mixture itself. Consequently, due to the inability to provide usable inputs to the required model, no determination of transportation and distribution between environmental compartments will be undertaken for tall oil and related compounds.

Summary of Environmental Fate Testing: Biodegradation data will be generated for four compounds in this category for which data are not already available. Photodegradation, hydrolysis and transport and distribution between environmental compartments are not applicable to these chemicals.

C. Evaluation of Existing Ecotoxicity Data and Proposed Testing

The basic ecotoxicity data that are part of the HPV Program include acute toxicity to fish, daphnia and algae. While there are existing data on these endpoints for some of the substances in this category, these data are conflicting and it is impossible to determine which, if any, of these findings are representative of ecotoxicity. The inconsistencies in how water samples were prepared for testing these endpoints render these data inadequate. Consequently, acute toxicity to fish, daphnia and alga will be retested for tall oil under conditions that maximize the solubility under the specific test exposure conditions, but reduce exposure to insoluble fractions that may cause nonspecific toxicological effects. In addition, the effect of both filtering to further minimize nonspecific physical effects, and of reducing the pH to the lower end of the acceptable range for test organism survival, will also be investigated for changes in toxicological effects. The results of preliminary tests will be used to select the most appropriate test conditions for the definitive test for each species.

Summary of Ecotoxicity Testing: The acute toxicity of tall oil to fish, daphnia and algae will be tested under conditions that maximize the solubility of the test material, but reduce exposure to insoluble fractions that may cause nonspecific toxicological effects.

D. Evaluation of Existing Human Health Effects Data and Proposed Testing

1. Acute Oral Toxicity

Acute oral toxicity studies investigate the effect(s) of a single exposure to a relatively high dose of a substance. This test is conducted by administering the test material to animals (typically rats or mice) in a single gavage dose. Harmonized EPA testing guidelines (August 1998) set the limit dose for acute oral toxicity studies at 2000 mg/kg body weight. If less than 50 percent mortality is observed at the limit dose, no further testing is needed. A test substance that shows no effects at the limit dose is considered essentially nontoxic. If compound-related mortality is observed, then further testing may be necessary.

Summary of Available Acute Oral Toxicity Data

Tall oil is non-toxic following acute oral exposure. The acute oral toxicity of tall oil has been determined in two studies in rats. The acute oral LD_{50} was > 5000 mg/kg in one study and > 6000 mg/kg in another study.

Summary of Acute Oral Toxicity Testing: Tall oil has been tested for acute oral toxicity and found to be non-toxic (i.e., LD_{50} > 5000 mg/kg) well above the guideline of 2000 mg/kg. Consequently, additional testing for this endpoint is not necessary.

Section 9 List of Attachments

Attachment 1, section 9: Forchem Product Data sheet

Attachment 2, section 9: Koski, Anna, Applicability of crude tall oil for wood protection**,** Faculty of Technology, Department of Process and Environmental Engineering, University of Oulu, University of Oulu, Finland, Acta Univ. Oul. C 293, 2008

Attachment 3, section 9: Method of analysis of Tall oil Product, Journal of the American Oil Chemists Society, Volume 36, Number 3/March 1959

Attachment 4, section 9: Dybdahl, H.P. 1993. Determination of log P_{ow} for single components in tall oil pitch.

Attachment 5, section 9: Safety Data Sheet Distilled Tal oil 20X,Forchem

Attachment 6, section 9: Zinkel and Russell 1989, Attachment 1, section 8 and Naval Stores Research at the Forest Products Laboratory, Past and Present.

Attachment 7, section 9: Tall Oil, Lars-Hugo Norlin, Bergvik Kemi, Sandarne, Sweden, 2005

Attachment 8, section 9: Gas chromatographic analysis of tall oil fractionation products after methylation with N,N- dimethylformamide dimethylacetal , McGuire J.M , Powis P.J.,Journal of chromatographic science 1998,vol 36,no.2,pp.104-108

Attachment 9, section 9: Wong,Arbokem Ink.,Vancouver,Canada,Cellulose Chemistry and Technology,36:388-37-88(2002):Degradation of crude tall oil held under heated conditions, Part1: Basic reactions and mixtures of model compounds Al Wong, ,Forest Chemicals Review,113(2):12-16,2003)

Attachment 10, section 9: Wong,Arbocem Ink.,Vancouver,Canada , Basic reactions and mixtures of model compounds Al ,Part 2 :Ternary mixture of model compounds and prediction of acid number decrease, Forest Chemicals Review,113(3):11-14,2003),

Attachment11,section 9 : Gerard R.Millet and Norman S.Thomson ,The reaction of tall oil Fatty Acids , the Institute of Paper Chemistry, Appleton, WISCONSIN, may, 1979

Attachment12,section 9 : Degradation of Tall Oil Fatty Acids by Molecular Oxygen in Alkaline Media ,The Institute of Paper Chemistry ,Gerrald R. Mittet

Attachment13, section 9: Charlie Scrimgeour, Scottish Crop Research Institute, Dundee,Scotland,Chemistry of Fatty Acids

Attachment 14, section 9: High Production Volume (HPV) Chemical Challenge Program , Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. 2001 .

Attachment 15, section 9 : High Production Volume (HPV) Chemical Challenge Program , Test Plan for Tall Oil and related substances, submitted to the US, EPA by the Pine Chemical Association , Inc. Aug. 2004

Refereces cited but not submitted:

Duncan DP (1989) Tall oil fatty acids. In: Zinkel DF & Russel J (eds) Naval stores: Production, chemistry and utilization. Pulp Chemical Association, New York, US: 346-439.

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Attachment 1, section 9

13 th November 2008

www.forchem.com

Product Data Sheet

For 20x

DEC 5 2008

for20x is special distilled tall oil (DTO) with the special features of fatty and rosin acids can offer.

for20x is an excellent raw material to be used in metal working fluids, oil field chemicals, soaps, cleaners and alkyd resins.

for20x is specially designed from carefully selected and distilled tall oils for outmost stability and low temperature properties.

Typical Analysis

Analysis	Typical value	Specification	Method
Acid value, mg (KOH)/1 g	192		ASTM D 465-01
Cloud point, °C	-1	6,5 max.	ASTM D 2500-99
Colour, Gardner (photometer)	4,5		ASTM D 6166-97
Relative Density at 20 °C	0,930		SCAN-T 2:65
Flash point, closed cup, °C	200		SCAN 6:67
Free fatty acids, %	75		ASTM D 1585-96
Free rosin acid, %	20	20±2	SCAN-T 14:78
Pour point, °C	-6		SCAN-T 5:67
Refractive index, n_D at 20 °C	1,485		SCAN-T 1:65
Saponification value	194		SCAN-T 12:72
Unsaponifiables, %	3		SCAN-T 13:74
Viscosity at 20 °C, cP (mPas)	80		ASTM D 2196-99

Delivery form	Deliveries in bulk by truck or ocean vessel. Liquid in road tanker, rail tank wagon, ISO-container, flexitank or 188 kgs net in steel drums.
EINECS number	232-304-6
CAS number	8002-26-4
CN-code	3803 00 90

Attachment 2, section 9

Koski, Anna, Applicability of crude tall oil for wood protection

Faculty of Technology, University of Oulu, P.O.Box 4000, FI-90014 University of Oulu, Finland,
Department of Process and Environmental Engineering, University of Oulu, P.O.Box 4300, FI-90014 University of Oulu, Finland

Acta Univ. Oul. C 293, 2008
Oulu, Finland

Abstract

Moisture content control is a very effective way of protecting timber. Treatments with environment-friendly, biodegradable tall oil are known to reduce the capillary water uptake of pine sapwood greatly, but despite the good results achieved there have been two problems that limit the use of tall oil for wood protection, the large amount of oil needed and the tendency for the oil to exude from the wood. This work was undertaken in order to obtain an understanding of the mechanism of wood protection by means of crude tall oil (CTO) and to find technical solutions to the main problems limiting its use for industrial wood protection.

It is shown that the emulsion technique is one way of solving the first problem, as it provides high water-repellent efficiency at considerably lower oil retention levels. The fact that water is used as a thinner in this technique instead of the commonly used organic solvents is beneficial from environmental, economic and safety points of view.

It is also shown that although the drying properties of CTO are inadequate for use as such in wood preservation, its oxidation and polymerization can be accelerated considerably by means of iron catalysts, which prevent the oil from exuding out of the wood. This also increases the water repellent efficiency of CTO treatment.

Most impregnation oils do not dry when applied in large quantities, because they hinder the diffusion of air through the wood, which supplies the necessary oxygen. Limiting of the oil uptake by the means of the emulsion technique disturbs the airflow to a lesser extent, and thus enhances the drying process. Hence, both the emulsion technique and the use of an iron catalyst improve both the water-repellent efficiency of tall oil treatment and the rate of drying of the oil, thus solving the two main problems related to wood impregnation with tall oil in one single-stage treatment which can be used in existing wood preservation plants. This is advantageous from both an industrial and an economic point of view.

Keywords: crude tall oil, emulsions, environment, moisture content control, wood protection

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C Technica 293

ANNA KOSKI

APPLICABILITY OF CRUDE TALL OIL FOR WOOD PROTECTION

Academic dissertation to be presented, with the assent of the Faculty of Technology of the University of Oulu, for public defence in Auditorium TA105, Linnanmaa, on February 15th, 2008, at 12 noon

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Abstract

Moisture content control is a very effective way of protecting timber. Treatments with environment-friendly, biodegradable tall oil are known to reduce the capillary water uptake of pine sapwood greatly, but despite the good results achieved there have been two problems that limit the use of tall oil for wood protection, the large amount of oil needed and the tendency for the oil to exude from the wood. This work was undertaken in order to obtain an understanding of the mechanism of wood protection by means of crude tall oil (CTO) and to find technical solutions to the main problems limiting its use for industrial wood protection.

It is shown that the emulsion technique is one way of solving the first problem, as it provides high water-repellent efficiency at considerably lower oil retention levels. The fact that water is used as a thinner in this technique instead of the commonly used organic solvents is beneficial from environmental, economic and safety points of view.

It is also shown that although the drying properties of CTO are inadequate for use as such in wood preservation, its oxidation and polymerization can be accelerated considerably by means of iron catalysts, which prevent the oil from exuding out of the wood. This also increases the water repellent efficiency of CTO treatment.

Most impregnation oils do not dry when applied in large quantities, because they hinder the diffusion of air through the wood, which supplies the necessary oxygen. Limiting of the oil uptake by the means of the emulsion technique disturbs the airflow to a lesser extent, and thus enhances the drying process. Hence, both the emulsion technique and the use of an iron catalyst improve both the water-repellent efficiency of tall oil treatment and the rate of drying of the oil, thus solving the two main problems related to wood impregnation with tall oil in one single-stage treatment which can be used in existing wood preservation plants. This is advantageous from both an industrial and an economic point of view.

Keywords: crude tall oil, emulsions, environment, moisture content control, wood protection

"And God said unto Noah, …
Make thee an ark of gopher wood; rooms shalt thou make in the ark, and shalt pitch it within and without with pitch."

(Gen. 6:13-14)

Dedicated to my baby daughter Maija

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Oulu, 8 January 2008 Anna Koski

List of original papers

This thesis is a summary of the work published in the following papers, which are referred to in the text by the following Roman numerals:

I Hyvönen A*, Piltonen P & Niinimäki J (2005) Biodegradable substances in wood protection. In: Jalkanen A & Nygren P (eds) Sustainable use of renewable natural resources – from principles to practices. University of Helsinki, Department of Forest Ecology Publications 34: 209-221.

II Hyvönen A*, Piltonen P & Niinimäki J (2006) Tall oil/water - emulsions as water repellents for Scots pine sapwood. Holz als Roh- und Werkstoff 64(1): 68-73.

III Hyvönen A*, Nelo M, Piltonen P, Hormi O & Niinimäki J (2007) Using iron catalyst to enhance the drying properties of crude tall oil-based wood preservative. Holz als Roh- und Werkstoff 65(2): 105-111.

IV Hyvönen A*, Piltonen P, Nelo M & Niinimäki J (2005) Wood protection of tomorrow – potential of modified crude tall oil formulations in wood protection. In: Meriläinen P, Sivula L & Oikari A (eds) Science for Sustainability. Proceedings of the Seventh Finnish Conference of Environmental Sciences, May 12-13, 2005, Jyväskylä. Finnish Society for Environmental Sciences. University of Jyväskylä: 35-38.

V Hyvönen A*, Nelo M, Piltonen P & Niinimäki J (2007) Using the emulsion technique and an iron catalyst to enhance the wood protection properties of tall oil. Holz als Roh- und Werkstoff 65(3): 247-249.

VI Vähäoja P, Piltonen P, Hyvönen A*, Niinimäki J, Jalonen J & Kuokkanen T (2005) Biodegradability studies of certain wood preservatives in groundwater as determined by the respirometric bod oxitop method. Water, Air & Soil Pollution 165(1-4): 313-324.

*Anna Koski née Hyvönen

The present author was the primary author of Papers I-V, and a co-author of Paper VI.

The first publication, Paper I, provides a review of wood protection with biodegradable substances, emphasizing the important role of water in wood deterioration and methods for protecting wood from moisture variations. The paper was written by the present author and modified in co-operation with the co-authors.

Paper II describes the designing and performing of the experiments together with the second author. The results were analysed and reported by the present author.

The designing and experimental work related to Paper III was carried out by the first two authors, and the reporting and analysis of the results and the writing of the paper were the work of the present author.

Paper IV describes the designing and performing of the laboratory experiments together with the second author, and again the results were analysed and reported by the present author.

The experiments reported in Paper V were designed and carried out by the present author together with the second and third authors. The present author was responsible for the analyses and reporting.

In Paper VI the present author participated in designing the experiments and reporting on them.

Contents

Abstract

1 Introduction

1.1 Background

Timber is a sustainable, economical, completely renewable, CO_2-neutral organic material which requires less energy to process than other construction materials. It is also a strong, aesthetically pleasing and highly durable material when properly maintained and used. But under certain conditions of exposure or use – and particularly when it becomes wet - it can decompose rapidly due to organic decay brought about by fungal micro-organisms in the presence of adequate moisture and air for an extended period of time (Sell & Leukens 1971) or to various effects of combinations of light, water, mechanical forces and heat, subsumed under the blanket term weathering (Anon. 1975). The deterioration of wood is thus caused by a combination of biological, chemical and physical processes, with water playing an important role in every case. The decay and discoloration caused by fungi, and to a lesser extent by bacteria, are a major source of loss in both timber production and the various uses of wood. To ensure a long, useful and safe life in certain end-use situations, timber needs protection from the hazards of fungal decay and weathering.

The classical concept of wood preservation is based on the principle of toxicity, i.e. impregnation with biocides (containing creosote, arsenic, zinc, copper, chromium, etc.) to prevent biological degradation. For environmental reasons, however, both traditional wood preservation and the use of natural tropical hardwood species are nowadays subject to political and consumer constraints. The European directive on the use of biocides places restrictions on the quantities of active substances, above all arsenic, that can be used in wood preservation, and their fields of application (EU 2003). Apart from the risks involved in using such materials, there is increasing concern over the problems entailed in disposing of the timber at the end of its commercial lifetime. Furthermore, wood treated with common preservatives is classified in Finland as hazardous waste (Ministry of the Environment 2001). These considerations have encouraged researchers and the wood protection industry to look for new alternatives.

Wood is an important resource for Europe, especially for the Nordic countries and Austria, where the forest cover has been expanding every year, and it has significant potential as a resource for the European bio-economy. Wood products are familiar to consumers and represent a sustainable life-cycle, but this also means that systems enhancing the durability of wood should be sustainable in terms of both their production and use. In addition to this, the treated wood products should at the end of their life be suitable for use as secondary fibre sources by related industries or for energy production by combustion or composting without involving any problems of residual chemicals arising from their treatment. The increased environmental awareness in recent years and the consequent spread of policies favouring the use of renewable resources and environment-friendly chemicals have led to an increased interest in "non-biocidal", more environment-friendly methods of wood protection, even the use of biodegradable substances. There is a growing need to develop technologically and economically reasonable solutions to this problem.

Wood extractives are known to be the principal source of natural decay resistance in wood (Scheffer & Cowling 1966), acting as natural wood preservatives, as it were, and the use of tall oil as a protective agent has been deemed promising because its precursors are extractives to be found especially in coniferous trees. Similar substances such as conifer pitch and tar have been used through the ages in shipbuilding, for instance. Tar production is known to have existed in Finland since before the 16th century, and tar became the most important export product for the Oulu region at one stage.

Fig. 1. A tar boat coming to the Koivukoski lock in Kajaani (Published by permission of the National Board of Antiquities).

The use of local timber species with enhanced qualities achieved by means of natural, domestically produced chemicals would be the ultimate solution to the need for environmentally friendly, protected wood products. Both crude tall oil and pine timber are produced a large quantities in Finland, although admittedly crude tall oil is of little use in its raw state at present and requires further distilling. By combining these Finnish resources – high quality pine timber and crude tall oil – it should be possible to create environment-friendly, biodegradable, durable and safe water-repellent wood products.

Our knowledge of wood preservation with tall oil is rather sparse, however, and more research is still needed. Before any real interest can be shown in the use of this substance for industrial wood protection, the problems limiting its use have to be solved.

This work was undertaken in order to improve the possibilities for exploiting crude tall oil for industrial wood protection. The aims were to obtain an understanding of the wood protection mechanism involved and to find technical solutions to the main problems limiting the use of tall oil for industrial wood protection.

1.2 The research challenge

Despite the good results achieved in wood protection with crude tall oil, there are two problems that limit its use on an industrial scale, the large amount of oil needed and the tendency for the oil to exude from the wood. The high retention levels increase the weight of the wood and may make it impractical and uneconomical to produce and use, while the tendency to exude from the wood arises from the high amounts of oil especially in the surface layers of the wood and because the lack of oxygen inside the wood prevents polymerization of the tall oil, causing the unpolymerized oil to exude with time to form a pitch-like surface. This restricts the applications of wood products treated with tall oil. It would be advantageous from an industrial and economic point of view if both these problems could be solved in a one single-stage treatment.

The most important driving forces behind this research and the reasons for undertaking it may be summed up as follows:

1. There is a need and demand for an environment-friendly wood protection method because of the banning of classical wood preservatives.
2. There is a need to develop technologies in which renewable materials are used rather than non-renewables, thus promoting sustainable development.
3. There is a need to increase our knowledge of the use of tall oil for wood preservation.
4. There is a lack of technical solutions to the main problems related to wood protection with tall oil from an industrial and economic point of view.

1.3 Initial assumptions

Once the problems to be considered had been identified, the next step was to focus the research appropriately. For practical purposes, this was done by making certain choices and assumptions beforehand. All the assumptions were nevertheless grounded in existing knowledge and common-sense demands that selected phenomena and processes should be implemented in mill-scale trials as well. The assumptions and their justifications were as follows:

1. In spite of the fact that there might be better alternatives among the natural oils for use as a wood protective agent, crude tall oil (CTO) was chosen for investigation here. Although about 2 million t of CTO is refined per year globally (Gullichsen & Lindeberg 1999), there is little use for it in its raw state today, so that it is distilled to tall oil fatty acids, tall oil rosin, tall oil heads and tall oil pitch. In their evaluation of the water-repellent properties of various oils, resins and waxes, Borgin and Corbett (1970a,b,c) found that no single component can meet all the requirements for a top-quality water repellent and concluded that the surface coatings or impregnants used for the treatment of wood must therefore be made from a blend of oils, resins and waxes. Unlike other natural oils, CTO already contains all the components needed for a good water repellent: oils, resins and waxes.
2. Scots pine sapwood was used in the experiments, as Finland has vast reserves of high-quality wood of this species. In addition, Scots pine is the only species that is impregnated in Finland, since spruce is very hard to impregnate and birch is less durable than pine even when impregnated.
3. Emphasis was to be placed on the simplicity and low cost of the treatment. It would be beneficial for the technical solutions to the main problems to be realizable in a single stage, cheap and suitable for use with the existing processes and equipment. Extra heating or expensive chemicals should be avoided.
4. Sustainability should be aimed at. The tall oil-based wood preservatives should obey the rules of green chemistry and engineering if they are to be sold as natural, environment-friendly products. The basic principle of green chemistry is that no harmful chemicals should be either used or generated when new products are designed, produced, used or discarded. Hence the raw materials and possible by-products involved in the production of the tall oil-based wood preservative should be harmless to the environment.
5. It would not be possible to test wood all the properties of the treated wood within this project, nor would it be necessary to do so. The contribution should be focused on the main issues: the water-repellent efficiency of the treatment and the drying properties of the oil.

1.4 The aims and hypotheses

The main hypothesis of the research reported here was as follows:

Crude tall oil (CTO) is an environmentally friendly, biodegradable substance that can be used for wood protection. The problems related to its use for this purpose can be solved in a technologically and economically reasonable manner while obeying the basic rules of green chemistry and engineering.

The aim of this thesis was to solve the problems related to wood protection with crude tall oil by testing the following sub-hypotheses:

1. The emulsion technique is a potential method for reducing the high quantities of oil required to protect wood from water uptake.
2. The oxidation rate of pure crude tall oil can be enhanced by means of iron catalysts, to the extent that its exudation from the wood can be prevented.
3. It is possible to enhance the drying properties of the emulsion oil phase and also maintain the high water-repellent efficiency, i.e. solve the two main problems related to wood impregnation with tall oil in one single-stage treatment.

1.5 Research environment and methodology

The experimental work was carried out in the form of laboratory tests at the Department of Process and Environmental Engineering and the Department of Chemistry, University of Oulu. The main step in this research was the design and construction of the experimental pressure impregnation equipment (Fig. 2), in which the most common wood impregnation processes used in industry could be performed under controlled conditions in order to ensure relevant conclusions.

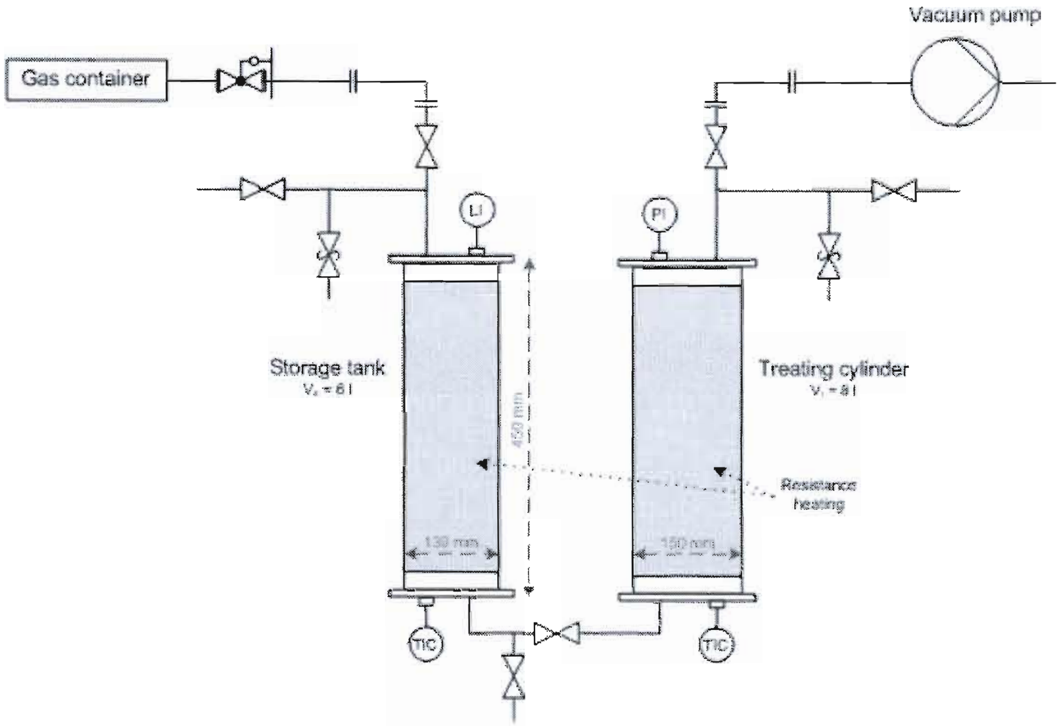

Fig. 2. The vacuum-pressure wood impregnation equipment.

There are various properties of the treated wood that could have been studied, but in order to keep the research reasonable in size only the most important ones were selected, mainly water-repellent efficiency and the drying behaviour of the oil. The details of the sampling and measurement arrangements are presented in each of the papers II-VI.

It is known, that both, wood and crude tall oil are a very heterogeneous materials. This heterogeneity of the wood matrix and crude tall oil mainly contributes to the chemical doses, reaction kinetics, energy efficiency of the emulsion production and impregnation time. However, the variations are not considered to have any significant influences on the main results of this thesis, and the conclusions of the research are applicable also to the industrial scale wood protection.

The general research methodology used here, which could apply irrespective of the subject studied, was based on the following main steps:

1. Identification of the problems,
2. Examination of the literature,
3. Selection of the background assumptions,
4. Statement of the hypothesis,
5. Testing of the hypothesis,
6. Discussion of the results,
7. Formulation of conclusions.

1.6 Results

The results of this doctoral thesis improve our understanding of wood protection with crude tall oil and extend our possibilities for using this method without encountering the problems that can arise from the high quantities of oil required or its exudation from the wood. The results can also be applied to other semi-drying oils. This work does not deal with all the problems related to this subject, and the solutions presented here are not the only ones.

1.7 Outline of the thesis

The experimental part of this work was designed to find solutions to the main problems limiting the use of tall oil for wood protection, as presented in Fig. 3. Paper I summarizes our existing knowledge of environment-friendly methods of wood protection and discusses the philosophy of the aim of wood protection nowadays. Paper II presents one solution to the first main problem, the large amount of oil needed. Paper III deals with the second problem, the tendency for oil to exude from the wood, and suggests a solution. The possibilities for combining the solutions presented in Papers II and III are examined in Papers IV and V, and finally the question of biodegradability, a very important property when developing environment-friendly wood protection methods or substances, is studied in Paper VI.

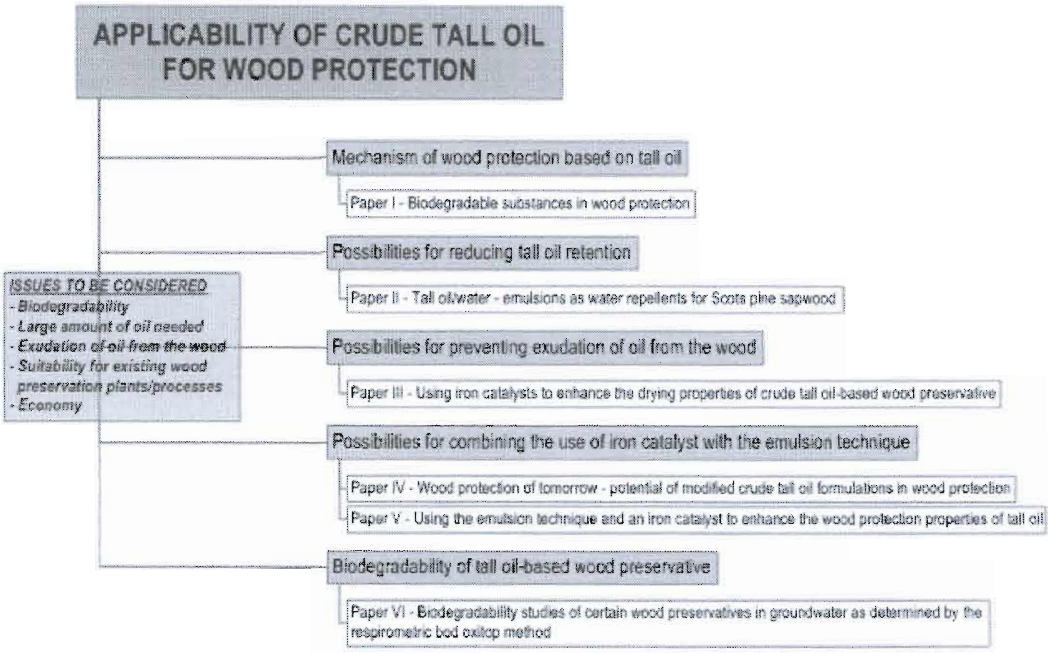

Fig. 3. Schema for the research – issues to be addressed and their distribution among the published papers.

The first chapter of this summary has described the research environment, the problems to be investigated and the initial assumptions. The purpose, history and main principles of wood preservation will be discussed in Chapter 2, while Chapter 3 will concentrate on the important role of water in wood deterioration and methods for protecting wood from moisture variations. Chapter 4 will focus on the use of crude tall oil for wood protection, introducing the problems related to its use and presenting alternative solutions to them. Other considerations relevant to the use of tall oil in wood protection will also be discussed. Most important findings will be summarized in Chapter 5, and recommendations for future work will be put forward in Chapter 6.

2 Prevention of wood deterioration

2.1 Purpose

Timber is a sustainable, economical, completely renewable, CO_2-neutral organic material which requires less energy to process than other construction materials. It is also a strong, aesthetically pleasing and highly durable material when properly maintained and used. But under certain conditions of exposure or use – and particularly when it becomes wet - it can be decompose rapidly due to organic decay or natural weathering agents.

Decay results from the action of fungal micro-organisms in the presence of adequate moisture and air for an extended period of time (Sell & Leukens 1971). The fungi that degrade wood may be classified as brown rot, white rot, soft rot, stain or mould according to the type of degradation they cause (Bowyer *et al.* 2003). Decay fungi (brown rot and white rot) cause significant softening or weakening of the wood, often to the point where its physical and mechanical characteristics are completely destroyed. Soft rot fungi typically attack wood that is very wet, and also weaken the wood and gradually degrade it from the surface inwards. Staining fungi create a bluish or blackish colour and thus detract from its appearance and value, but they do not have a serious effect on its strength or physical integrity. Moulds occur only on exposed surfaces and may discolour products in use, but do not affect their strength.

Weathering is a blanket term that covers the various effects of combinations of light, water, mechanical forces and heat (Anon. 1975). The process occurs through photo-oxidation of the surface catalyzed by the ultraviolet (UV) radiation in sunlight, and it is increased by other processes such as washing by rain, changes in temperature, changes in moisture content and abrasion by windblown particles. The weathering of wood involves changes in colour, roughening and checking of the surfaces, loss of surface fibres and warping. (Anon. 1975, Anon. 1999, Feist 1983)

Thus the deterioration of wood is caused by a combination of biological, chemical and physical processes, with water playing an important role in every case. The decay and discoloration caused by fungi, and to a lesser extent by bacteria, are the major source of loss in both timber production and the various uses of wood. To ensure a long, useful and safe life in certain end-use situations, timber needs protection from the hazards of fungal decay and weathering.

Improved utility has been the purpose of wood protection since man first supported wooden structures on stones to keep them dry or daubed wood with oil of cedar to prevent its decay. Construction techniques that keep the wood dry still remain the most important practice for preserving wood, while chemical or modification treatments make its use possible under an increasing variety of conditions. Preservatives make wood toxic to organisms that might use it for food or shelter, while water repellents and dimensional stabilizers retard the moisture changes that may take place in wood, fireproofing agents reduce the spread of flames and prevent the wood from supporting its own combustion, while other chemicals or treatments modify its characteristics for special applications. The increasing interest in aesthetics has favoured treatments that enhance the natural beauty of wood. All these treatments may be said to enable wood to compete successfully with other materials on the commercial markets.

Wood preservation can greatly increase the serviceability of wood, although we should not forget the philosophy regarding the durability of materials expressed by Clark in 1868:

> *"Though sometimes, in ignorance, the perishable character of all surrounding things may be lamented, yet on the other hand, it must not be forgotten that perpetual destruction and perpetual renewal are in reality the essential causes of all life, beauty and harmony."*

The degradable nature of wood, treated or untreated, may prove in the long run to be its greatest asset (Graham 1973). Although it is a perishable material, this can be seen as an advantage, in that it can be disposed of in the environment at the end of its useful life (Hill 2006). Its molecular constituents are broken down by natural processes and assimilated into nutrients. It is obviously not desirable, however, that this should occur while the wood is still in use.

2.2 History of wood protection

2.2.1 Stories of the Great Flood

> *"And God said unto Noah, ...*
>
> *Make thee an ark of gopher wood; rooms shalt thou make in the ark, and shalt pitch it within and without with pitch."*
>
> (Gen. 6:13-14)

> *"Some carried pitch, and some carried oil.*
> *Some carried timber, and some carried nails.*
> *Some cut wood, and some nailed wood.*
> *Sixty lengths by sixty lengths the boat did grow.*
> *Six decks below, six decks above, twelve decks in all.*
> *I drafted plans, I showed where each board should go.*
> *I showed where pitch must go.*
> *Three times we pitched the outside in the seams.*
> *Three times inside in the seams."*
>
> *"Pitch for the hull I poured into the kiln*
> *and ordered three full volumes of oil*
> *to start with and two times three more yet.*
> *For what is security?"*
>
> (Translations of Gilgamesh, TABLET XI, Column II)

Perhaps the oldest records of wood preservation can be found in the stories of the Great Flood sent by God, or the gods, to destroy civilization as an act of divine retribution, a widespread theme in the world's cultures past and present. The stories of Noah and his pitched ark in the Book of Genesis, and Utnapishtim's pitched ship in the Epic of Gilgamesh are among the most familiar versions of these myths. The latter comes to us from Ancient Sumerian and was originally written on 12 clay tablets in cuneiform script. It describes the adventures of the historical King of Uruk (somewhere between 2750 and 2500 BC). The most complete version of the epic was preserved on eleven clay tablets in the collection of the Assyrian King Ashurbanipal, who lived in the 7th century BC. It is considered to be the oldest recorded piece of literature (Fig. 4). (See Dundes 1988, Encyclopædia Britannica 2006, Wikipedia 2006.)

Fig. 4. The "Deluge Tablet" (Tablet 11) of the Epic of Gilgamesh in Akkadian (© Trustees of the British Museum).

2.2.2 Development of wood technology 2000 BC – 1750 AD

The following early historical records of the development of wood technology have been collected mostly by Robert D. Graham (1973), and also by Roger M. Rowell (2006a, 2006b), Osmo Suolahti (1961) and Panu Kaila (2000).

In ancient Africa the natives would harden their wooden spears by placing a straight, sharpened wooden stick on the glowing coals and then pounding the burnt end with a rock, repeating this process many times until the end was sharp and hard. It took thousands of years before it was understood that it was pyrolysis of the hemicelluloses, producing furan resins, which, combined with carbon and compression, resulted in this extremely hard composite (Rowell 2006a, 2006b).

The ancient Egyptians took advantage of the tremendous swelling pressure of wood when using dry-to-wet wooden wedges to split giant granite boulders from the side of a quarry for their obelisks (Rowell 2006a, 2006b).

The Vikings burned the outside of their ships to make them water-resistant, without knowing anything about hydrophobicity or the insulating properties of charred wood (Rowell 2006a, 2006b).

In the eastern part of the Mediterranean around 2000 BC the first ploughs were being used to cultivate the land, the potter's wheel was coming into widespread use, metallurgy was developing, writing and the early alphabets were emerging, and sea trading was becoming well established. Wooden ships had become the principal means of transportation and were to remain so for nearly 4000 years. The continued expansion of population and shipping around the shores of the Mediterranean during the next thousand years inevitably led to a scarcity of durable shipbuilding timber and a need emerged for the preservation of non-durable species.

In the Nile Valley the early Egyptian belief in life after death led to the erection of huge stone monuments and equally monumental efforts to preserve the bodies of men and animals, and also wood, by daubing with natural oils.

The rise of Greece about 1000 BC was accompanied by the increasing use of durable wood and the development of construction practises aimed at keeping the wood dry, either by placing wooden pillars on stones, or by placing stones on top of the pillars to shield them from rain.

By 72 AD the records of Pliny the Elder, an early Roman naturalist, show that a basis for wood technology and preservation had been established. The susceptibility of sapwood to rotting had been recognized, for instance, as had its vulnerability to woodworm, the durability of cypress, cedar, ebony, lotus, box, yew and juniper, which do not age or experience decay, and it had been observed that trees under the water of the Red Sea could remain free of rot for 200 years and that timber that was well smeared with cedar oil did not suffer from maggots or decay. A Roman architect recorded use of the lees of oil to preserve timber from all manner of worms, noted that pitch would defend it against water and recounted that a wooden tower that had been thoroughly daubed with alum would not catch fire when under siege.

There are also historical records of wood preservation on the other side of the world. It is known that the Chinese treated timber with sea water or salt water thousands of years ago in order to increase its durability (Suolahti 1961).

Marine borers were reported in 1560 to have caused damage to wooden piles in the earthen dykes of Holland, and the damage was so extensive by 1700 as to threaten the inundation of the country. 100 ships of the Spanish Armada were destroyed by shipworm in the West Indies in 1590, and at one stage the Royal

Navy in Great Britain was faced with a timber shortage that was aggravated by external (marine borers) and internal decay (dry rot). The general introduction of copper sheathing into the Navy during the American Revolution finally put an end to the external threat, but dry rot remained unmastered to the end. Albion (1926) noted that the timber problem was prominent among the causes of the delays which furthered the progress of American independence. The interest in wood preservation which had been stimulated by the frantic search for solutions to timber problems during the 200 years for which national survival rested heavily on the durability of wooden ships was stimulated further in the early 1800s and maintained for another 100 years by the search for suitable preservatives for railway sleepers (Graham 1973).

The records of wood protection in Northern Europe include references to the famous 17th century German chemist Glauber, who treated wood by carbonizing it and then tarring it, and finally immersing it in wood acid. In the mid-18th century it was noticed in Sweden that the logs in a copper mine had become free of decay on account of their contact with a vitriol solution (Kaila 2000). Copper or iron vitriol is still used as a additive/preservative in the traditional Swedish red paint.

2.2.3 The Industrial Revolution

A period of significant advances in the industrial processing of wood occurred during the Industrial Revolution, the major technological, socioeconomic and cultural change that began in Britain in the late 18th and early 19th century and spread throughout the world. Among these advances was the construction of railways, which created a need for sleepers for the tracks and points. In addition, the development of telecommunications led to a need for telegraph poles. As industrial technology advanced, wood was used more frequently in exterior structural applications. Species of wood that did not possess inherent resistance properties proved unsuitable for these purposes, however, due to biological attack, creating a need for preservative treatments. Above all, the maintenance of the huge, expanding railway systems led to the recognition of the need for more durable sleepers (Freeman *et al.* 2003, Graham 1973).

2.2.4 The development of wood preservatives

The earliest U.S. patent for a wood preservative was issued to Dr. Wm. Crook in 1716 for "...Oyle or Spirit of Tarr..." Mercuric chloride and copper sulphate were also first recommended during the 18^{th} century, while zinc chloride was proposed as a wood preservative in 1815 (Freeman *et al.* 2003). The early patents dealt primarily with poisonous substances and coatings to shield wood from the effects of water.

The development of more effective wood preservatives demanded an explanation for how these chemicals could protect wood from fungi. The dangers entailed in some treatments became all too apparent from one experiment in which green railway sleepers were treated by placing a dry powder containing salt, arsenic and mercuric chloride in holes in the wood. The arsenic and corrosive sublimate effloresced from the ties, and when cattle came and licked them because of the salt they died, so that the track was strewn with dead cattle for kilometres on end (Graham 1973).

The use of coal tar creosote was patented by Franz Moll in 1836. Creosote oil had originally been used to preserve meat on sea voyages (Greek *kreas sozo*, meat preservative), but it was already being used to protect wooden ships by 1796. In the early 19^{th} century creosote was made from beech wood tar, and its distillation from coal tar started later. Because of the expansion of the railways creosote became one of the most widely used wood preservatives in the world. (Freeman *et al.* 2003, Kaila 2000)

Copper naphthenate has been used as a wood preservative since 1889. It was first used in Germany and has been in commercial use since 1911. Another historically important preservative, patented in 1928, is pentachlorophenol (PCP or Penta), a crystalline compound formed in the reaction of chlorine with phenol. It is a widely used oil-borne preservative (Freeman *et al.* 2003).

The story of CCA began in 1933, when an Indian timber engineer, Sonti Kamesam, made a discovery that saved the lives of countless coal miners: that the injection of arsenic and copper into timber beams will prevent them from rotting. Arsenic, a classical poison, kills wood-eating insects, while copper kills fungi. Kamesam's special trick was to add chromium to this formula, thereby binding the two toxic metals to the wood cell walls. The result was stronger roofs in the damp underground tunnels through which coal was extracted. Kamesam's invention not only extended the life expectancy of miners in India but it also saved money and trees. CCA has been the major preservative in use since that time. (Anon. 1986, Cooper 1999, Kamesam 1934, Murphy 1998, Steingraber 2004)

Another major arsenic-based preservative, ammoniacal copper arsenate (ACA) was standardized in 1950 and was modified in the 1980s by replacing some of the arsenic with zinc, to yield ACZA (Freeman *et al.* 2003).

The Osmose Wood Impregnating Company was started by Dr. Carl Schmittutz in the early 1930s to exploit patents on a preservative process using sodium fluoride, potassium bichromate, sodium arsenate and dinitrophenol, known in the industry as FCAP (fluor chrome arsenate phenol). Penetration of these preservatives into green wood or wood of high moisture content was achieved through a process of diffusion, or osmosis. One early commercial use of this preservative in the U.S. was a timber dipping and stacking process used at coal mines. (McNamara 1990, Osmose 2006)

Borates are a group of old preservatives that were rediscovered in the 1980s, including salts such as sodium octaborate, sodium tetraborate, and sodium pentaborate, which are dissolved in water. Boron compounds offer some of the most effective and versatile wood preservative systems available today, combining the properties of broad-spectrum efficacy against decay, fungi and insects with low mammalian toxicity. The stumbling block is that they remain soluble in water and readily leach out of the treated wood if it gets wet. (Anon. 1986, Anon. 2005, Borax 2006)

Recent restrictions on the use of toxic preservatives (EU 2003) have led the wood preservation industry to develop a range of substitutes based on organic or inorganic formulations, such as alkaline copper quaternary ammonium compounds (ACQ), copper azoles (CBA-A, CA-B) and copper-HDO (Anon. 2004). General opinion is that there are problems related to the stability of copper within the wood, however.

Legislation is now moving towards the registration of wood preservative chemicals (REACH regulations, EU 2006), with certain requirements placed upon determination of the environmental impacts of their use (Hill 2006). These requirements will inevitably lead towards increased costs in the development of new biocides, and it is most unlikely that any of these will be developed specifically for wood preservation.

2.2.5 Development of treatment processes

Timber preservation has a long history, but it has only developed as an industry over the last two centuries. The industrial revolution and innovations such as Stephenson's locomotive led to the development of pressure vessels, and in 1831 a method for applying wood preservative by pressure in a sealed iron vessel was patented by a Frenchman named Bréant. Prior to this most preservatives were applied by a simple brush-on method. (Hughes 2004) The first successful preserving process, Kyanizing, introduced by Kyan (1832) for use in the early treatment plants in the United States, involved the soaking of wood, canvas or rope in dilute aqueous solutions of mercuric chloride. In the Margary process (1837), wood was soaked in solutions of copper sulphate, but it was the Burnett process (1838), in which wood was impregnated with zinc chloride in water under pressure, that eventually became the principal method for treating railway sleepers in the U.S. until the 1920s. (Graham 1973)

A pressure impregnation process for the application of the coal-tar creosote patented by Moll in 1836 was in turn patented by John Bethell in 1838. Known as the Bethell, or full-cell process, it was the first significant use of pressure for wood treating operations and marked a major step forward in wood preservation history (Freeman *et al.* 2003). This process, which became the basis for the present-day pressure-based wood preserving industry, employs an initial vacuum period followed by filling of the cylinder with preservative and a further pressure period to inject it. A modern-day modification, the modified full-cell (Fig. 5), employs an initial vacuum of lower intensity and shorter duration along with a final vacuum period. The name "full-cell" is derived from the fact that the wood cells are full of preservative at the end of the process. There are five distinct stages in the modified full cell process (as presented in Anon. 1986 and Anon. 1988, for instance):

1. *Initial vacuum.* The timber is loaded into the treatment vessel, which is sealed. An initial vacuum withdraws air from the wood cells, minimizing their resistance to the entry of the preservative. Most treatment specifications require a vacuum of 80–85% (0.15–0.2 bar) to be maintained for between 15 minutes, for small-dimension, permeable timber, and one hour, for large-dimension, less permeable timber.
2. *Flooding with preservative.* The treatment vessel and timber are flooded with preservative while the vacuum is maintained.

3. *Pressure period.* The vacuum is then released and a hydraulic pressure of between 10 and 16 bar is applied by means of a pump and maintained for the time specified in the treatment schedule. Alternatively, the pressure is maintained until the required amount of preservative to achieve the specified retention level has been forced deep into the wood. The pressure period can range from 1 to 3.5 hours depending on the dimensions and permeability of the timber. If the timber is such that there is difficulty in obtaining the desired uptake, the treatment is continued to the point of "refusal", i.e. the pressure is maintained until no further preservative is taken up by the timber.
4. *Preservative drain.* The pressure is released and the remaining preservative transferred from the treatment vessel to the storage tank.
5. *Final vacuum.* The treatment vessel is evacuated and the vacuum released when the gauge reaches 0.15–0.2 bar, or after 15 minutes, whichever occurs first. This final vacuum will remove excess preservative from the surface layer of the wood and reduce any dripping which might occur when the treated timber is removed from the cylinder.

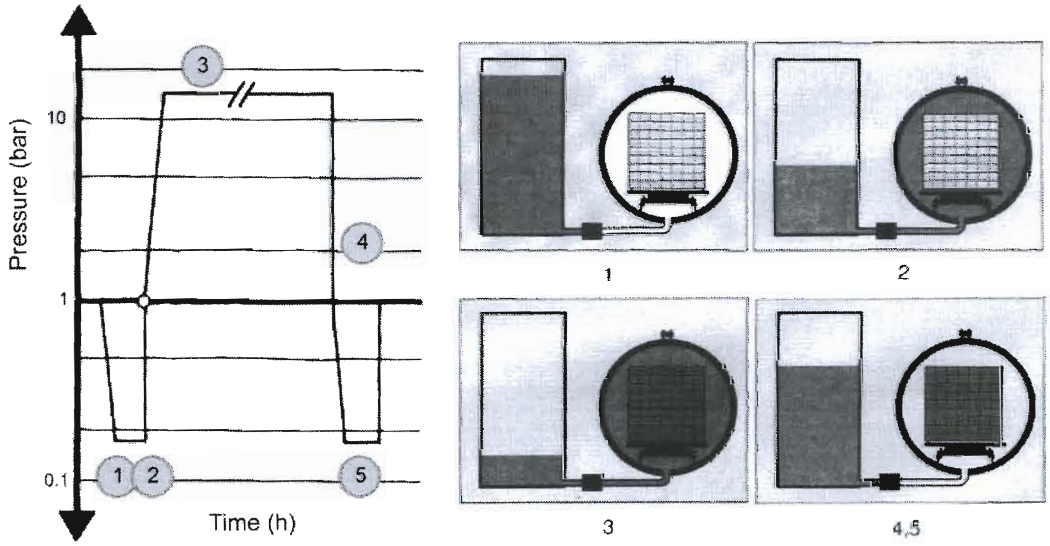

Fig. 5. Diagrams of the full cell vacuum pressure impregnation process (modified from Anon. 1988 (left), Anon. 1986 (right)).

Several wood treating processes and some new chemicals were introduced in the following decades. The Boucherie Process developed in 1839 provided the basis for modern-day sap displacement methods and is still used in Europe. In sap displacement the preservative is applied to one end of the log via a cap which fits over the end (Anon. 1986). Pressure is applied to the cap which forces the preservative along the log, while the sap is pushed out at the other end. In 1874 Julius Rütgers of Mannheim, Germany, developed a process for treating wood with zinc chloride and creosote, which was later modified by J.B. Card and used to treat railway sleepers until the mid-1920s. Other full-cell treatment methods were developed in the late 19th and early 20th centuries but are no longer in use. Boulton published his classic work "On the Antiseptic Treatment of Timber" in 1884, providing the basis for the Boultonizing process for seasoning wood, or Boulton drying. (Freeman *et al.* 2003)

With the high price of creosote oil making the related process expensive, an empty-cell process was developed by Max Rüping of Germany and patented in 1902. This employs an initial application of air pressure before filling the cylinder and a higher pressure to inject the preservative. After release of the pressure, the air in the wood cells expands and the excess preservative in the cell lumen is "kicked back", resulting in a much lower level of retention than in conventional full-cell treatment. A vacuum period applied after removal of preservative solution completes process. This step reduces the amount of entrapped air and hence the bleeding of preservative, yielding a much cleaner treatment. A second empty-cell treatment, patented by C.B. Lowry in 1906, has atmospheric pressure as the initial air pressure, and when the pressure is released after the pressure period, the air in the lumen expands, forcing the preservative out and leaving the lumen almost empty, although the cell walls are thoroughly treated. Both processes provide for the impregnation of wood with relatively large amounts of creosote and subsequent withdrawal of part of the oil, giving a lower final retention of preservative than in the Bethell Process. The empty-cell process is used when deeper penetration but less retention is required. (Anon. 1986, Freeman *et al.* 2003, Graham 1973)

Many modifications to the basic full-cell and empty-cell processes have been used to treat wood. The Oscillating Pressure Method (OPM), employing rapid cyclical oscillations between vacuum and pressure, has been used to treat refractory wood species, while a multi-Lowry process, the Alternating Pressure Method (APM), was developed to treat green or partially seasoned wood with CCA. The High Pressure (HP) method was developed in Australia to treat railway sleepers at high pressure (69 bar). The Pulsation Process is similar to the APM Process except that the pressure is never fully reduced to atmospheric during the cycle and is increased during each oscillation. The use of an overlaying oil treatment on wood already treated with waterborne preservatives constitutes the Royal Process that is in use in Scandinavia, and approaches such as the MSU Process, the Multiple-Phase Pressure (MPP) Process, the MCI Process, the Cellon and the Dow Processes have also been introduced. (Freeman *et al.* 2003) The Vacuum Processes (e.g. the Double Vacuum Process) are used for the controlled application of organic solvent preservatives to building timber in millwork applications and to produce inexpensive fence posts. These processes are essentially similar to high-pressure full-cell treatment except that a lower vacuum and pressure can be used because the organic solvent preservative readily penetrates the timber (Anon. 1986).

2.3 Principles of wood preservation

The prevention of wood degradation is based on the idea of interfering with the basic physiological requirements for the growth and development of microorganisms, including (Fig. 6): favourable temperatures, an adequate supply of oxygen, at least a certain amount of moisture, suitable nutrition, and certain essential growth factors or vitamin and mineral constituents (Stamm 1964). If steps can be taken to ensure that any of these requirements fails to be met, the risk of attack by wood degrading organisms will be eliminated.

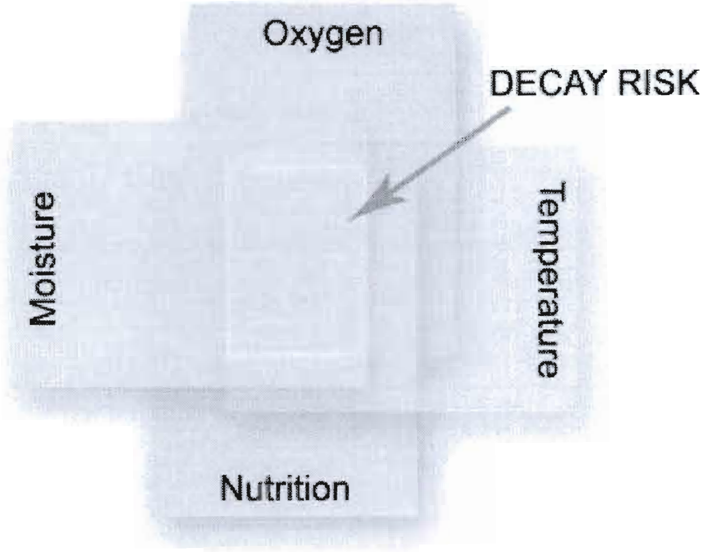

Fig. 6. Factors contributing to the risk of wood decay (modified from Anon. 1988).

The classical concept of wood preservation is based on the principle of toxicity (elimination of suitable nutrition), while impregnation with biocides (containing creosote, arsenic, zinc, copper or chromium, for example) will prevent biological degradation. The European directive on the use of biocides places restrictions on the quantities of active substances, above all arsenic, that can be used in wood preservation and their fields of application (EU 2003). The wood treatment industry in the US and Canada have also begun a transition away from CCA, as the Environmental Protecting Agency (EPA) in the US and Health Canada's Pest Management Regulatory Agency (PMRA) have banned the use of CCA preservatives containing arsenic in residual structures as of 1st January 2004 (EPA 2006, PMRA 2005). Furthermore, wood treated with common preservatives is classified in Finland as hazardous waste (Ministry of the Environment 2001). Apart from the risks involved in using such materials for treatment purposes, there is increasing concern over problems appearing in the disposal of timber after the end of its commercial lifetime. Systems enhancing the durability of wood should be sustainable in both production and use. In addition to this, treated wood products should at the end of their life be suitable for energy production by combustion or composting, or for use as a secondary fibre source by related industries, without presenting any problems related to residual chemicals from their treatment.

It is possible, however, to use other methods than the application of toxic chemicals to ensure that conditions do not meet the basic requirements of microorganisms. Controlling the temperature or removing the oxygen supply are generally not good practical means of preventing the deterioration of wood, but control of the moisture content by restricting the wetting of wood is a more practical and effective means of protection. The water availability to fungi influences the wood deterioration process to a large extent and is therefore the most important factor in wood conservation.

3 Treatments to reduce wood/water interactions

3.1 Wood/water interaction

3.1.1 General

The wood cell walls are mainly composed of polymers with hydroxyl or other oxygen-containing groups which attract moisture through hydrogen bonding. Lignin (to a small degree), hemicelluloses, the non-crystalline portion of the cellulose, and the surfaces of the cellulose crystallites are all responsible for moisture uptake in wood. Three forms of water exist in wood:

- free water,
- bound water, and
- water vapour.

Free water, or capillarity water (Fig. 7), is the liquid water that fills the lumen, the driving force for which is absorption by capillary action, which is comparable to the way a sponge soaks up water. These water molecules are not bound to the wood. Bound water is found in the cell wall, where it is adsorbed through the attraction of water molecules to the hydroxyl groups and bound to these groups through either monomolecular or polymolecular adsorption, implying that either one or more water molecules may be bound to a single hydroxyl group (Fig. 8). The bonding is stronger in monomolecular adsorption than in polymolecular adsorption, so that it takes more effort to remove the last water molecule from a hydroxyl group. Water vapour is water in its gaseous phase, which is located in the cell lumina and cavities within the cell walls. (Banks 1973, Bowyer *et al.* 2003, Siau 1971, Skaar 1988)

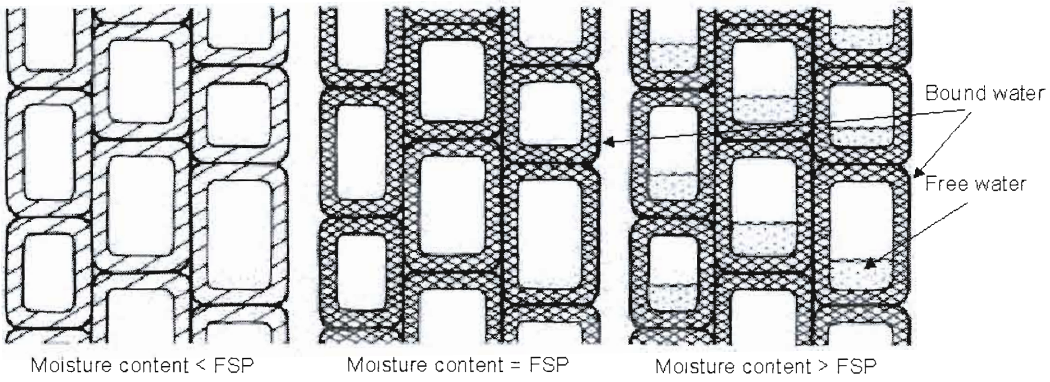

Fig. 7. Examples of the moisture content of wood (modified from Anon. 1988).

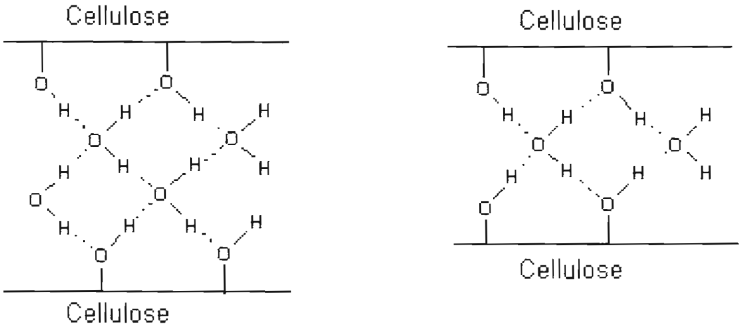

Fig. 8. Polymolecular and monomolecular bonding of water to the cellulose chain.

The amount of water in wood or a wood product is usually termed the moisture content (MC) and is defined as the weight of the water expressed as a percentage of the moisture-free or oven-dry (OD) weight of the wood.

$$MC = \frac{(m_w - m_d)}{m_d} \times 100\%, \qquad (1)$$

where

MC is the moisture content (%),
m_w is the weight of wet wood (g),
m_d is the weight of dry wood (g).

As water is adsorbed into it, the cell wall increases in volume almost proportionally to the volume of water added (Stamm 1964). This swelling increases until the cell wall is saturated with water (fibre saturation point, FSP), see Fig. 7. Any water available beyond this point will remain as free water in the void structure and not cause any further swelling. This process is reversible, since below the fibre saturation point wood shrinks as it loses moisture. Wood is an anisotropic material, which means that it shrinks and swells to different extents in three anatomical directions (Fig. 9), shrinking most in the direction of the annual growth rings (tangentially), about one-half as much across the rings (radially) and only slightly along the grain (longitudinally) (Anon. 1999). As the S_2 layer of the wood cell wall is generally thicker than the other layers combined, the molecular orientation of this layer largely determines how shrinking occurs. Most of the chain molecules in the S_2 layer are oriented almost in parallel to the long axis of the cell (with microfibril angles of 10-30°). When water enters between the cellulose chains in the S_2 layer it forces the chains apart, causing transverse (radial and tangential) swelling, while any change in the longitudinal direction will be minor. (Bowyer *et al.* 2003, Siau 1984) Stresses will arise in the wood due to moisture gradients between the surface and the interior, and unbalanced stresses can result in surface warping, twisting and checking.

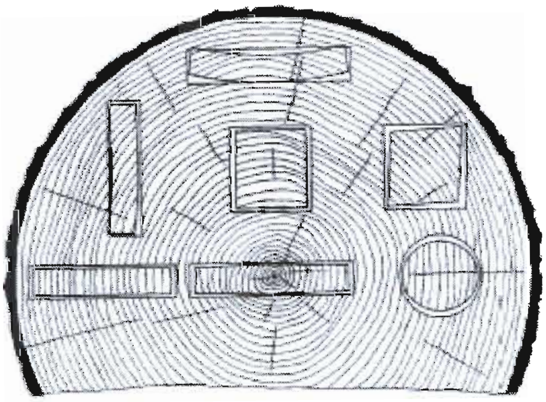

Fig. 9. Characteristic shrinkage and distortion of portions of a log of wood as affected by the direction of the growth rings (Anon. 1999).

3.1.2 Contact angle

The necessary conditions for existence of a contact angle were first stated by Thomas Young in 1805. An attractive force exists between a solid and a liquid in contact with it, the net value of this force being determined by the relative magnitudes of the cohesive forces within the liquid and the adhesive forces generated between the solid and liquid. Where the adhesion of the liquid to the solid is equal to or greater than the cohesion of the liquid, a drop of liquid implanted onto the solid will spread spontaneously. The angle between the solid and the liquid at the solid/liquid/air interface, termed the contact angle, will then be zero. If the liquid/solid adhesion is less than the liquid cohesion, the drop of liquid will not spread but will stand on the surface, making a finite contact angle with it (Fig. 10). Contact angle between water and a treated surface is the most direct indicator of water repellency, the tendency for the surface to resist interaction with water (Rowell & Banks 1985).

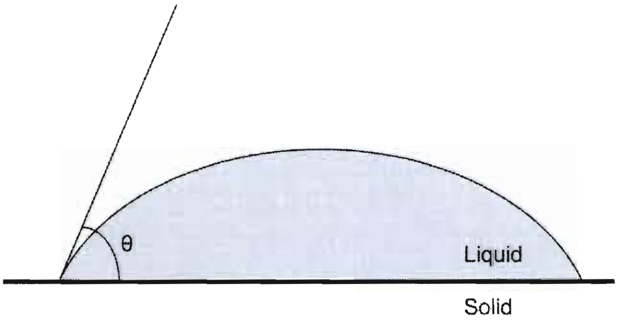

Fig. 10. Contact angle between a drop of liquid and a solid surface.

3.1.3 Capillary pressure and the Kelvin equation

Wood is a capillary porous medium, the pore structure of which is defined by the lumina of the cells and the cell wall openings (pits) interconnecting with them (Fig. 11). The main routes for liquid penetration are provided by these capillaries.

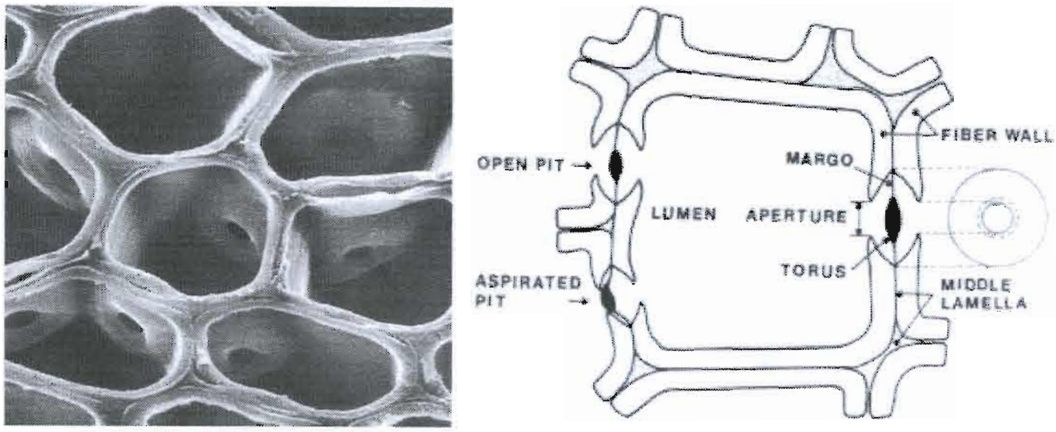

Fig. 11. Intertracheid conifer bordered pits, left (Butterfield & Meylan 1980), and cross-section of a tracheid showing open and aspirated bordered pits, right (Ilvessalo-Pfäffli 1995, modified from Knuchel 1954).

With the exception of the unique case where the contact angle (θ) is equal to 90° ($\cos\theta = 0$), any liquid contained in a cylindrical capillary of uniform bore will have a curved surface. The pressure difference, or capillary pressure (P_C), across this curved surface can be defined by Jurin's equation, derived from the Kelvin equation (Adam 1963):

$$P_C = \frac{-2\gamma_L \cos\theta}{r}, \tag{2}$$

where

P_C is the capillary pressure,
γ_L is the liquid surface tension,
θ is the liquid/solid contact angle,
r is the capillary radius.

The pressure gradient set up by the pressure difference acts so that liquid is forced into the capillary spontaneously for θ values less than 90°, while conversely, when θ is greater than 90° an external pressure larger than P_C must be applied to drive liquid into the capillary (Adam 1963, Rowell & Banks 1985). Although the structure of wood departs significantly from a simple cylindrical capillary model, the general principles of capillary penetration hold and the magnitude of P_C remains functionally related to the cosine of the contact angle (Adam 1963).

In systems involving water as the liquid phase, surfaces forming contact angles of less than 90° are said to be wettable or hydrophilic, whereas those giving rise to contact angles greater than 90° are said to be water-repellent or hydrophobic (Rowell & Banks 1985).

3.1.4 Wood moisture content and decaying fungi

Fungi can only cause serious damage to wood when the moisture content is above the fibre saturation level (26% to 32% of the dry wood weight, depending on species). This amount of moisture cannot be acquired as water vapour absorbed from humid air, however, as the moisture content of wood exposed only to atmospheric water vapour normally ranges from 8% to 15% (Levi 1973), but can only exist in green wood or as a result of exposure to liquid water. Wood is protected very effectively from deterioration as long as its moisture content is maintained below its fibre saturation point (FSP). Optimal wood moisture levels for most wood-degrading fungi lie between 40% and 80% (Scheffer 1973). Another important factor is the availability of the water in the wood to the fungi. Water activity (a_w), which is defined as the vapour pressure of water over the substrate divided by the vapour pressure of pure water, can be used to determine to what extent the water can be used by the fungi (Griffin 1981, Zabel & Morrell 1992).

According to the general rule set out by Cartwright and Findley (1958), microbiological degradation can occur only if the wood has a moisture content exceeding 20% of its oven-dry weight. Although this is substantially below the approximate 30% minimum required for fungal decay, a lower moisture content still is advisable, because this provides a margin of safety in the event of the material not drying uniformly (Scheffer 1973). The most widely used and effective means of protecting wood is to dry it soon after it comes from the tree, and thereafter to take appropriate precautions to keep it dry when handling it and making use of it. When a safe moisture content cannot reasonably be assured, treatment with preservatives, surface coatings or water repellents is usually the logical alternative.

3.2 Treatment methods

In order to stabilize wood as far as possible, it must be protected from moisture variations. Various structural and chemical methods can be used to accomplish this, at least in theory. It was already known in Greece around 1000 BC that wooden pillars can be kept dry by mounting them on stones. This is structural wood protection, or wood protection by design. One widely used structural method involves surface coatings, although the most successful involve the application of water repellents and dimensional stabilizers.

Rowell and Banks (1985) divided treatments designed to reduce the tendency for wood to take on moisture and change its dimensions into two categories: water repellents and dimensional stabilizers. The effectiveness of a water repellency treatment can be defined as its ability to prevent or control the rate of liquid water uptake in both the cell wall and the capillaries. In contrast, the effectiveness of a dimensional stabilizing treatment can be defined as its ability to reduce the swelling and shrinking of wood due to moisture absorption. Since only water that has penetrated into the cell wall can cause swelling, free liquid water in the capillaries is permissible. Dimensional stability depends more on the extent than the rate of water uptake, and some treatments can reduce both swelling of the wood and the rate of water uptake. Typical swelling trends over time for untreated and hypothetically treated wood specimens are shown in Fig. 12 (Rowell & Banks 1985). The upper curve shows how an untreated specimen will quickly take up water through capillary action and swell to its maximum extent, while the lower curve shows the theoretical impact on a treated wood specimen. The reduced rate of water uptake indicates increased water repellency, while the reduced extent of swelling indicates greater dimensional stability.

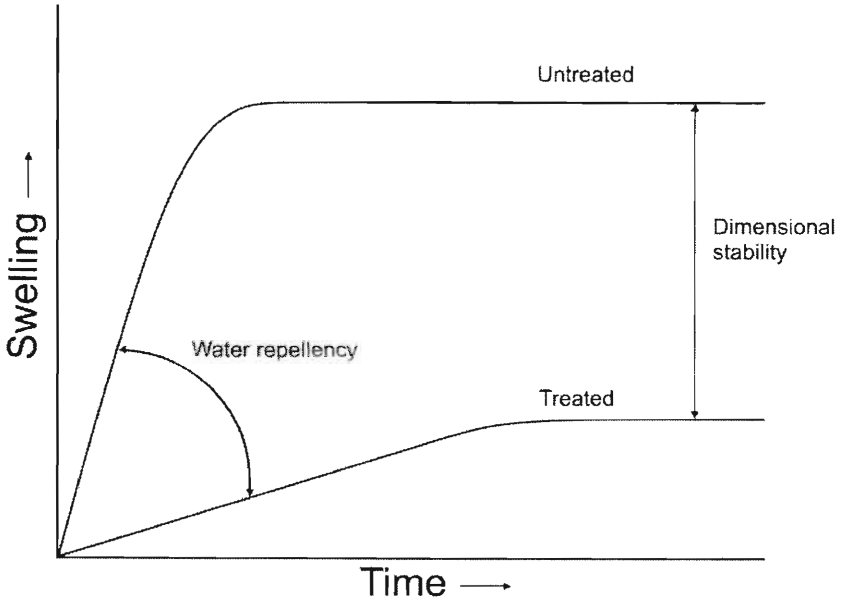

Fig. 12. Hypothetical swelling over time for water repellency and dimensional stability treatments (modified from Rowell & Banks 1985).

Treatments for water repellency and dimensional stability can be further classified into the three types as shown in Fig. 13 (Rowell & Banks 1985). Type I treatments reduce the rate of moisture uptake but the extent of swelling is ultimately nearly the same as for untreated wood. Such a treatment would improve water repellency but not dimensional stability. Type II reduces the extent of swelling but not the rate at which the wood takes up moisture. This would improve dimensional stability but not water repellency. A type III treatment, on the other hand, will reduce both the extent and the rate of swelling and improves both water repellency and dimensional stability.

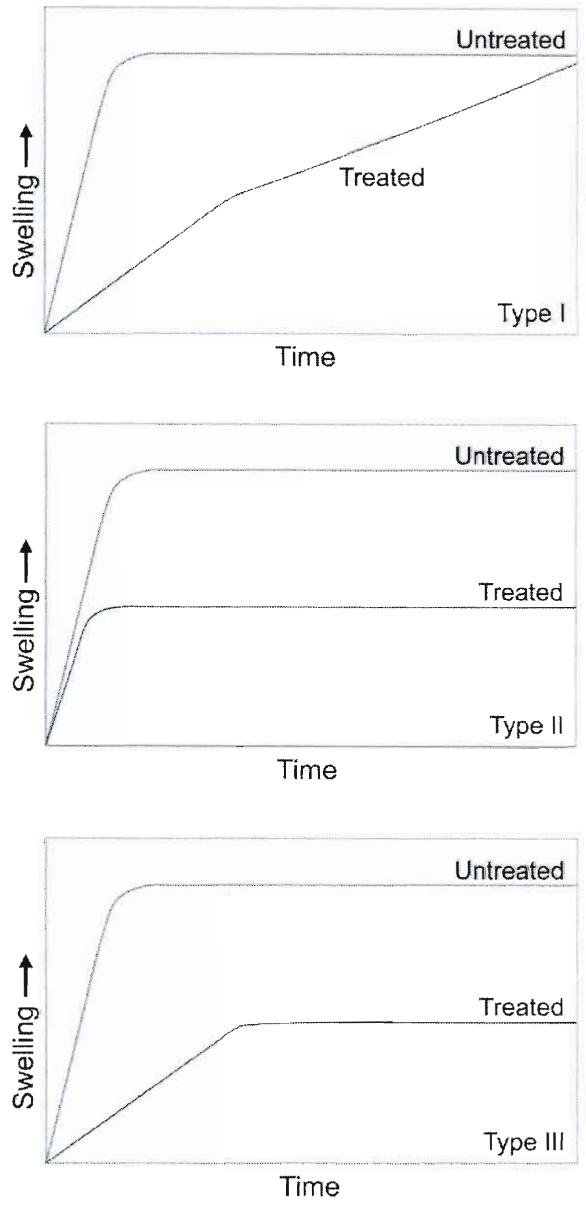

Fig. 13. Hypothetical wood treatments for: water repellency (type I), dimensional stability (type II), water repellency and dimensional stability (type III) (re-drawn from Rowell & Banks 1985).

The principles of intervention in wood-water interactions are illustrated in Fig. 14, in which the cases (untreated and treated wood) are presented simply at the lumen and cell wall level. In an untreated cell wall the water molecules absorbed into the wood settle between the wood polymers, forming hydrogen bonds between the hydroxyl groups and the individual water molecules. In addition to the division of treatments into water repellents and dimensional stabilizers (Rowell & Banks 1985), Sailer and van Etten (2004) distinguished two principal types of treatment: those which do not cause changes within the cell walls of the wood and those which do cause changes. The latter are also known as wood modification treatments.

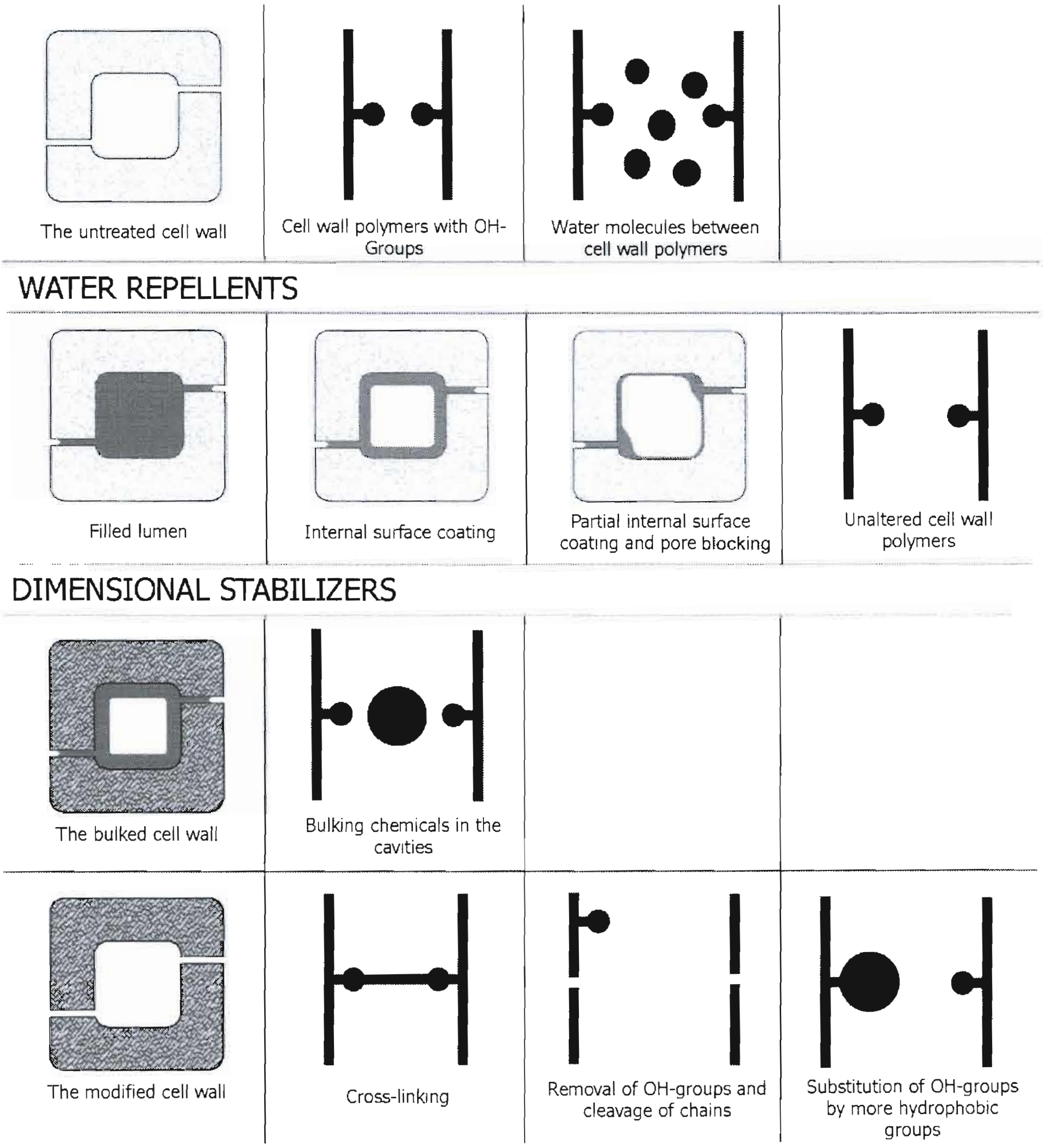

Fig. 14. Forms of intervention in wood-water relations (modified from van Eckeveld 2001).

3.2.1 *Surface coatings*

The use of surface coatings is based on the formation of a surface film of polymeric material such as varnish, lacquer or paint. As long as the coating film is perfect and has no cracks, openings or other imperfections, water will not penetrate into the wood - or at least any penetration will be very slow, depending on the permeability of the film to liquid water or water vapour. In practice, however, there is no such thing as a perfect film. Microscopic cracks develop more or less rapidly depending on the severity of exposure to weathering. Once a crack has developed, nothing can stop the penetration of water, which in most cases lifts the surrounding film, widens the cracks and accelerates the destruction of the film (Borgin 1961).

The main reason for this destructive process is the phenomenon of preferential wetting: water has much higher affinity for wood than does the coating film. As a result, the stronger wood-water hydrogen bonding displaces the weakly bonded film deposits from the wood surface. This type of process is to a certain extent dependent on the mechanical strength of the film, but it cannot be prevented if the wood is exposed to water for a sufficiently long time (Borgin 1961).

3.2.2 *Dimensional stabilizers*

While effective as water repellent treatments in some cases, external and internal coatings give only low dimensional stability. There are many ways of controlling the dimensional changes in wood, ranging from species and geometric selection through cross-lamination and the reduction of hygroscopicity to various chemical methods (Rowell & Banks 1985).

By combining all the art and science of wood recorded from ancient times up to the present (see section 2.2.2, Development of wood technology 2000 BC – 1750 AD), it has been discovered that if you change the chemistry of wood you change its properties, and that leads to a change in performance. It was on this foundation that the science of chemical modification was born (Rowell 2006a).

A treatment that reduces the tendency for wood to take on water may result in a reduction in the extent of cell wall water uptake, and thus in a reduction in shrinking and swelling. Optimal treatments of this type would remove the hydroxyl groups from the cell wall polymers, and thus remove the sites for hydrogen bonding to water (Fig. 14). Removal of the hydroxyl groups is theoretically possible through reductive reactions; but these would destroy the wood (Rowell & Banks 1985).

In the chemical modification process the timber is treated with a chemical that produces changes in its cellular structure (Anon. 2003a), either by new chemical bonding within that structure (the direct method), or by blocking chemical and physical processes with a non-bonded material (the indirect method). The hydroxyl groups play the leading role in many chemical modification reactions, i.e. the chemical added to the wood participates in a reaction with a hydroxyl group within the wood structure. In this case the wood reacts in the manner of an alcohol. The result is a strong covalent bond (similar to the bonds holding the atoms in the wood together), which is fairly stable. This produces a new form within the wood structure and alters the properties of the original material. Modification may lead to the reduction of OH groups, cell wall bulking (which leaves the cell wall permanently swollen), cross-linking and/or undesired cleavage of the chains. The decrease in the number of accessible OH groups leads to limited interaction with water and improved dimensional stability. Often the treated wood is no longer recognised as a nutrient medium by the enzyme systems of degrading fungi, or else the lowered equilibrium moisture content no longer promotes decay (Homan & Jorissen 2004). However, chemical treatments involve the risk of damage to the wood as a result of unfavourable process parameters or aggressive agents such as alkaline or acidic catalysts (Donath 2004).

Many chemicals have been used to modify wood. The main reaction types are: chemical cross-linking, where the structural units of the wood cell walls are bound together chemically, polymerizing addition, in which the chemicals react with a hydroxyl group and then polymerize, and single-site addition, where the chemicals react with a single hydroxyl group (Anon. 2003, Rowell & Banks 1985).

Acetylation is one of the most thoroughly examined chemical wood modification methods, the processes involved in which were described early in the 20th century. First performed by Fuchs in Germany in 1928, the process results in the substitution of the wood hydroxyl groups by acetyl groups. This is a single-sided addition reaction, which means that one acetyl group replaces one hydroxyl group, with no polymerization. As a result, the wood is less hygroscopic. It is also known that acetylation is able to impart a significant degree of decay resistance to wood, although considerably less is known about the mechanism(s) by which this takes place. One hypothesis is that acetylation changes the chemical nature of the wood substrate, in that hydrophilic OH groups are replaced by acetyl groups, and as a consequence various fungal enzyme systems are no longer capable of recognizing the substrate and hence cannot break down the wood cell wall polymers. In addition, acetylation improves the UV resistance of wood without changing its original colour. (Hill 2006, Homan & Jorissen 2004, Rowell 2006a, Rowell 2006b, Stamm 1964)

Furfurylation (modification with furfuryl alcohol resin) is also known to be an efficient method of obtaining wood products of high dimensional stability. Furfuryl alcohol is a renewable chemical derived from furfural, produced from hydrolysed biomass waste (e.g. bagasses, molasses, sugar canes, corn cobs, sunflowers, or birch chips). The acid catalyst reaction chemistry of furfuryl alcohol in wood is very complex in nature, and the reaction results in a densely branched and cross-linked furan polymer linked to the wood cell wall polymers. (Goldstein 1960, Hill 2006, Homan & Jorissen 2004)

A wide range of silicon compounds (silicons, siloxanes, silanes) are available on the market for use as hydrophobation agents, for instance, but they are also suitable for wood modification. Various studies have shown that it is possible to modify wood by impregnation with silicon compounds, leading to a subsequent reaction (see Donath 2004, Donath *et al.* 2006a, Donath *et al.* 2006b, Hill 2006, Sèbe & DeJéso 2000). It is known, for example, that both the water repellent efficiency of the treatment and its antifungal effect can be increased with multifunctional silane systems containing alkyl and amino groups (Donath *et al.* 2006b).

Instead of using a chemical to produce a change in the wood structure, it is also possible to use heat to effect changes. This is called heat treatment, or thermal wood modification. Most of the thermal treatments involve controlled pyrolysis, the wood being heated (> 180°C) in the absence of oxygen (O_2), but there are various processes (the Thermowood process in Finland, the Plato process in Holland, the Retification and Perdure processes in France, and the Oil heat treatment in Germany) which are either performed in gaseous atmospheres (nitrogen, oxygen, water steam) or in oil (rape seed oil, linseed oil or sunflower oil) at temperatures between 150°C and 250°C. The mechanism imparting a reduction in hygroscopicity is partial degradation of the hemicellulose components of the wood cell wall and to some extent of cellulose and lignin. The reduced number of free hydroxyl groups makes the wood cell structure less accessible to water, and heat treatment also lowers the equilibrium moisture content, improves dimensional stability and promotes resistance to wood-destroying fungi. These changes are dependent on the temperature used and the length of the treatment period, but the more effective the treatment is in altering the above-mentioned properties, the greater will be the loss in terms of the strength properties of the wood. (Stamm 1964, Viitaniemi & Jämsä 1996; Syrjänen 2001, Jämsä & Viitaniemi 2001, Militz & Treerdsma 2001, Vernois 2001, Rapp & Sailer 2001, Homan & Jorissen 2004, Hill 2006)

There are many other wood modification methods in existence in addition to those mentioned above, but acetylation, furfurylation and heat treatment are the ones with the greatest potential inform an industrial point of view. There has been considerable commercial activity in the commodity product wood modification sector over the past decade, largely focused in Europe, reflecting the changes in the legislative climate affecting the wood protection industry (Hill 2006). Thermal wood modification has been commercialised in Finland, Holland, France and Germany at least, acetylation in Holland and Sweden and furfurylation in Norway.

3.2.3 Water repellents

The rate of water uptake can be considerably reduced either by providing a water barrier, or by rendering the wood hydrophobic, although very few materials are truly hydrophobic (Borgin & Corbett 1970a). Depending on the amounts used, water repellents applied to wood fill in the cell lumina or are deposited on the external pore surfaces and to some extent on the internal ones (Fig. 14) and thereby impart hydrophobic properties to the wood surface. This means that water cannot spontaneously penetrate the wood pores through capillary action and the rate of water absorption is thus limited (Banks & Voulgaridis 1980). It is not possible to make the cell wall inert to water without wood modification, however. Also, wood treated with water repellent and exposed to water will swell to the same extent as untreated wood in the course of time. Although water repellents do not stop all water absorption, they are an excellent treatment for wood used out of doors, because they inhibit the absorption of liquid water at times of rain while still allowing the wood to dry after rain (Anon. 1999). The reduction in the average moisture content and the period of time when the wood is wet enough to allow attack by micro-organisms will slow down the rate of fungal attack (Stamm 1964, Feist & Mraz 1978). Bacterial attack is favoured by the presence of free water, and a certain amount of free water is necessary for optimal fungal growth (Rowell & Banks 1985).

An idealized model of wood treated with water repellent would be an envelope of cells evenly coated with a hydrophobic layer surrounding an untreated core. As the surfaces of the cells within the treated zone are hydrophobic, liquid water is unable to penetrate unless an external pressure greater than the capillary pressure is applied (Rowell & Banks 1985). Theoretically, a coherent monomolecular layer should be sufficient to induce this effect (Razzaque 1982). Provided the hydrophobic layer remains intact, deep penetration of the wood with the hydrophobic deposit should be unnecessary. In practice, however, it has been found that deeper or complete impregnation leads to a more durable effect (Borgin 1965). This is probably due to the fact that the deposit in immediate contact with the water source is gradually degraded. Where deep impregnation is achieved, fresh, undegraded deposits are continually being exposed, offering extended protection (Razzaque 1982).

Water repellents are usually non-chemically bonded, complex blends of various materials such as waxes, oils, natural or synthetic resins, fungicides or insecticides and solvents (Borgin & Corbett 1970a, Feist & Mraz 1978, Razzaque 1982, Williams & Feist 1999). They are applied to wood, usually by immersion or vacuum impregnation, as solutions in organic solvents (Rowell & Banks 1985). According to Razzaque (1982) these water repellent substances seem to be bonded to the cell wall only by relatively weak Van der Wall forces.

Several researchers, including Banks & Voulgaridis (1980) and Feist & Mraz (1978), have shown that the treatment of wood with non-chemically bonded water repellents of this kind gives significant control over water uptake for a reasonable period of time. Banks and Voulgaridis (1980) reported that the eventual loss of water repellent effectiveness may be associated with failure of the bond between the cell wall and the deposit, resulting largely from degradation of the wood surface. The phenomenon of preferential wetting as described above may also occur in wood treated with water repellent. When the water repellent material is exposed to water for a sufficient length of time, the hydrophobic substances will be displaced by the water, thus detracting from the performance of the treatment. The weak Van der Waals wood-deposit bond is then replaced by a stronger wood-water hydrogen bond (Banks 1973, Razzaque 1982).

The promising effect of water repellents in preventing wood from reaching high moisture contents led to the development of preservative-water repellent mixtures (Archer & Cui 1997, Belford & Nicholson 1969, Cui & Archer 1997, Fowlie *et al.* 1990 and Zahora & Rector 1990). By adding water repellents to the common wood preservatives, more dimensionally stable products with reduced moisture variations and increased biological durability can be achieved. Moreover, the leaching of toxic preservatives into the environment can be reduced (Treu *et al.* 2004). The Royal treatment process, developed by Bror Olof Häger, represents a combination of this kind, as it consists of a period of impregnation with a water-soluble preservative followed by an oil impregnation period (Treu *et al.* 2001).

3.2.4 Environment-friendly, biodegradable water repellents

Many water repellents, like the classical wood preservatives, have the drawback of being detrimental to the environment. Increased environmental awareness in recent years, and the consequent spread of policies favouring the use of renewable resources and environment-friendly chemicals, have led to increased interest in "non-biocidal", more environment-friendly wood protection methods, even the use of biodegradable substances. The term "non-biocidal" includes natural oils, waxes, silicones, resins, polymers, chemical modification and heat treatments (Militz 2001). Our present knowledge of the use of biodegradable substances for wood protection is summarized in Paper I.

Biodegradable substances are often associated with environment-friendly products, which can be broken down by natural processes into more basic, innocuous components. Such products are usually broken down by bacteria, fungi or other simple organisms. If substances are very toxic to these organisms, biodegradation is not possible. According to this definition most chemicals are ultimately biodegradable, but the rate of breakdown varies considerably. The rate is not as important, however, as what the product breaks down into. The ideal final products of any complex would be carbon dioxide (CO_2) and water (H_2O), but where many more complex chemicals are concerned this is difficult. The banned hazardous and toxic pesticide DDT, for example, is biodegradable, although only rather slowly, but a more serious problem is that its breakdown products, DDD and DDE, are even more toxic and dangerous than the original DDT. Thus, even though a product may be biodegradable, it may not be environment-friendly (Anon. 2002, Anon. 2003b). In the present context, therefore, the term "thoroughly biodegradable substance" may be taken to mean a substance which breaks down completely, and whose breakdown products are not toxic.

More environment-friendly water repellents such as extractives from trees and natural resins have been successfully tested in the laboratory (Voulgaridis

1993, Voulgaridis 2001, Passialis & Voulgaridis 1999, Var & Öktem 1999, Voulgaridis & Passialis 1999), and studies have been undertaken to investigate the water repellency and dimensional stability of wood treated with natural oils (Anon. 1999b, Borgin 1961, Borgin & Corbett 1970, Paajanen *et al.* 1999, Van Eckeveld 2001, Van Eckeveld *et al.* 2001a, Van Eckeveld *et al.* 2001b) and the biological efficacy of these substances (Anon. 1999b, Jermer *et al.* 1993, Sailer *et al.* 1998, Paajanen *et al.* 1999, Ritschkoff *et al.* 1999, Van Acker *et al.* 1999, Sailer & Rapp 2001). Natural oils appear to be capable of preventing water uptake by wood, and their chemical and physical composition is promising (Sailer *et al.* 2000). In addition, unsaturated oils (such as drying oils) can oxidize when exposed to oxygen from the air (Porter *et al.* 1981, Porter & Wujek 1984), which results in a more protective layer on the surface of the wood. The most commonly studied natural oils available for wood protection purposes have been linseed oil and tall oil.

Natural oils can be divided into drying, semi-drying and non-drying oils. Drying oils such as linseed oil oxidize to form a tough elastic film when exposed to air, semi-drying oils oxidize more slowly and will polymerize in the course of time due to reactions with oxygen, but the oil film usually remains tacky, while non-drying oils do not dry or form a film even on lengthy exposure to air. The degree of unsaturation in an oil determines its drying characteristics and can be found by adding iodine (I_2). The iodine value (IV) of an oil is the amount of iodine required to saturate its double bonds (g I_2/100 g oil). High iodine values > 140 are typical of drying oils, and low ones < 125 of non-drying oils, with the iodine values of semi-drying oils lying between the two (Wicks *et al.* 1992). Tall oil is a semi-drying oil, the typical iodine value of its fatty acids being 125-130, or somewhat less for crude tall oil. This indicates slow drying. The greatest difference between these two common natural oils that can be used for wood protection purposes, linseed oil and tall oil, is that linseed oil contains much greater amounts of polyunsaturated fatty acids such as linolenic and linoleic acid. Polyunsaturated fatty acids are considerably more reactive than monounsaturated fatty acids, mainly because their alpha hydrogens are much more acidic.

Environment-friendly, biodegradable substances are highly suitable for wood protection when the aim is to prevent moisture uptake by the wood, as they enable the wood moisture content to be kept below 20%, which does not meet the requirements for wood degradation by fungi. These substances cannot compete with biocides in terms of the biological durability of wood that is in contact with the ground or with water, however (Hazard class 4 in EN 335-1/2/3), where moisture levels in the wood are permanently over 20%. If one wants a product as durable as biocide-treated wood, and maybe also maintenance-free, the structural material may have to be plastic, steel, aluminium or concrete, for instance. But then the price might be higher. On the other hand, there is a demand for environment-friendly wood products that are created from renewable raw materials using sustainable, clean production methods even though the product is not so durable. Some form of compromise has to be made.

In spite of the fact that there might be better (at least better drying) alternatives among the natural oils for use as a wood protective agent, crude tall oil (CTO) was chosen for examination here. Little use can be found for CTO in its raw state today, so that it is mostly distilled further. In their evaluation of the water-repelling properties of various oils, resins and waxes, Borgin and Corbett (1970a, b, c) found that no single component can fulfil all the requirements for a top quality water repellent and concluded that the surface coatings or impregnants used for the treatment of wood must therefore be made from a blend of oils, resins and waxes. Unlike other natural oils, CTO already contains all these.

4 Crude tall oil for wood protection

4.1 General

4.1.1 Sources, production and utilization of crude tall oil

Crude tall oil (CTO) is a major chemical by-product of the kraft pulp industry. Its name comes from the Swedish word for pine, "tall", and indicates that the primary source is pine. During the kraft pulping process based on coniferous wood some of the extractives (resin and fatty acids) released from the wood react with the alkaline pulping liquor to form sodium soaps. These soaps dissolve in the pulping liquor but float to the surface upon concentration of the liquor. The tall oil soap is separated from the black liquor by skimming and is further treated with sulphuric acid to form CTO (see Drew & Propst 1981, Gullichsen & Lindeberg 1999, McSweeney 1989, McSweeney *et al.* 1987).

The average yield of CTO is in the range of 30-50 kg/t of pulp, which corresponds to 50-70% of the initial amount in the raw material used for pulping (Alen 2000). This CTO is a saleable product for a pulping mill, but represents only about 1-1.5% of the mill's total revenue (Gullichsen & Lindeberg 1999). With the closing of the circulations in kraft pulp mills, the role of the CTO plant has become more important, as it is a major source of sulphur for addition to the process and a part of the mill's waste handling and removal system. The availability of tall oil for a mill is greatly dependent on the wood species used for pulping, the growth conditions of the trees and the method and duration of storage of the logs and chips. Even among extractives-rich pine species, however, there is significant variation in the availability of tall oil (see Alen 2000, Drew & Propst 1981, Gullichsen & Lindeberg 1999, Holmbom & Ekman 1978, McSweeney 1989, McSweeney *et al.* 1987).

About 2 million t of CTO are refined globally per year (Gullichsen & Lindeberg 1999). There is little use for it in its raw state today, but it is purified and fractioned by vacuum distillation to the yield following base products (Fig. 15):

- tall oil fatty acids (TOFA),
- tall oil rosin (TOR),
- distilled tall oil (DTO),
- tall oil heads, and
- tall oil pitch.

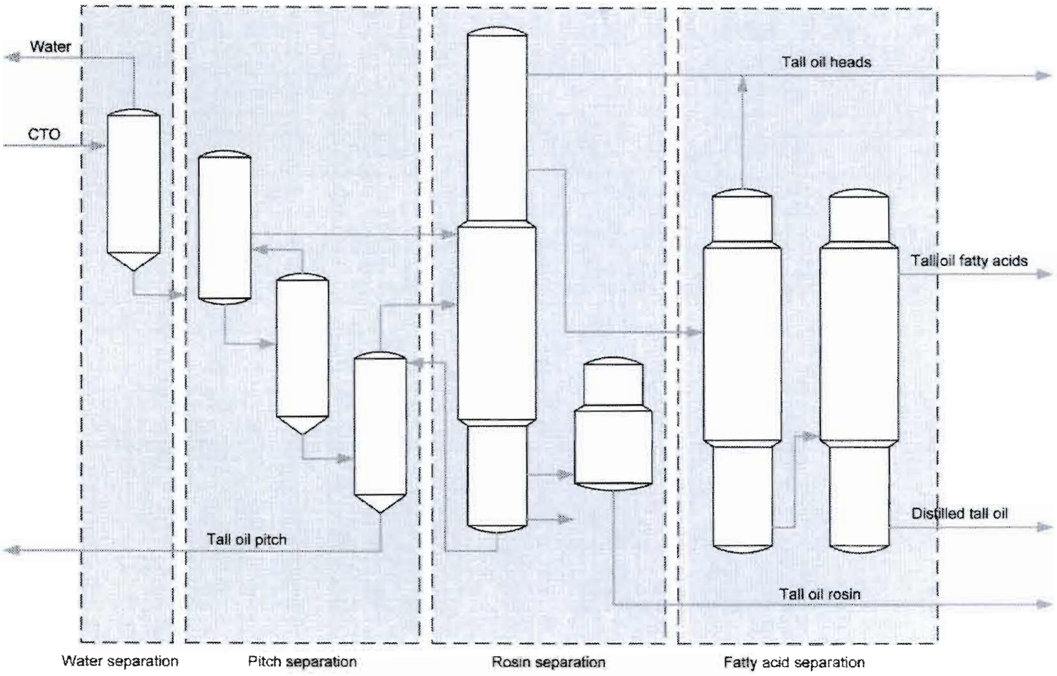

Fig. 15. Simplified diagram of the tall oil distillation process (modified from Anon. 2006, McSweeney *et al.* 1987, McSweeney 1989)

Tall oil products have a wide range of applications, and the various base products can be further refined into a wide variety of products and formulations. Tall oil fatty acids are used in paint vehicles, soaps/detergents, printing inks, foam inhibition agents, lubricants, greases, flotation agents and industrial oils. Tall oil rosin has traditionally been used as a paper size, but this use is declining. Other applications include alkyd resins, printing inks, adhesives, emulsifiers, paint and lacquer vehicles and soaps. Tall oil pitch has some special applications as an asphalt additive and in rust protection, printing inks and oil-well drilling muds, but its primary use is still as a sulphur-free fuel. (Alen 2000, Gullichsen & Lindeberg 1999)

CTO can also be used as a lime kiln fuel, which is an attractive alternative when it is of poor quality. It can replace the primary fuel oil partially or totally and has almost the same heat value and combustion properties (Gullichsen & Lindeberg 1999). Emission trading has further increased the attractiveness of this alternative nowadays.

4.1.2 Chemical composition and characterization of crude tall oil

The dark-coloured crude tall oil (CTO) is not composed of pure triglycerides like other vegetable oils, but is rather a mixture of fatty acids, rosin acids and unsaponifiable substances, e.g. sterols, waxes and hydrocarbons. The precursors of CTO are the extractives found especially in coniferous trees. Pine typically contains extractives such as free resin acids, fatty acids in the form of glycerides, and terpenes. The extractives also contain neutrals or unsaponifiables that are primarily alcohols of various kinds.

Several carboxylic acids, fatty acids and rosin acids are found in crude tall oil. The predominant fatty acids, contributing the bulk of the observed physical and chemical properties, are oleic and linoleic acids (Duncan 1989), whereas the main resin acids are abietic-type acids and pimaric-type acids (Soltes & Zinkel 1989), see Figs. 16 and 17.

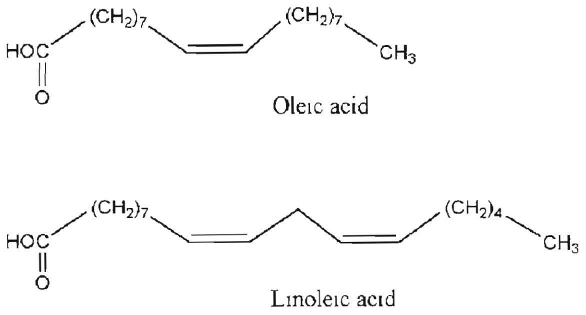

Fig. 16. Fatty acids.

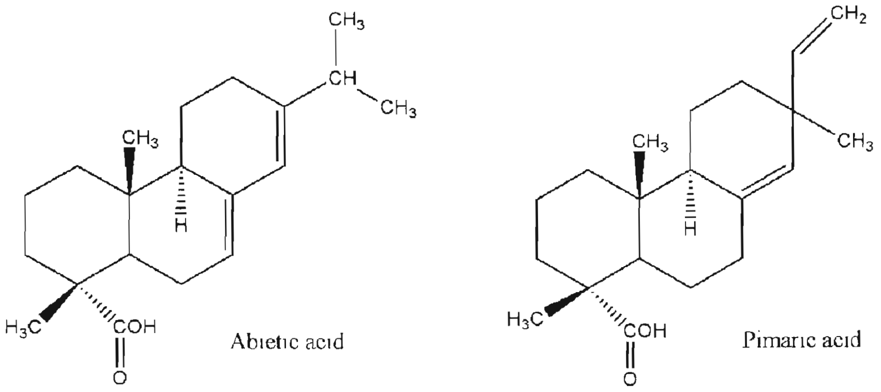

Fig. 17. Resin acids.

CTO varies considerably in composition and quality depending on the location of the mill, time of year, growing cycle of the tree, tree species, ageing of the wood, amount of heartwood, pulping conditions, handling and storage of the wood and the efficiency of the system used to recover the tall oil (see Drew & Propst 1981, Gullichsen & Lindeberg 1999). Furthermore, storage of CTO leads to esterification of the sterols and other alcohols with fatty acids (Holmbom 1978, Holmbom & Avela 1971a, Holmbom & Avela 1971b, Holmbom & Stenius 2000), which will reduces the number of acids it contains and increase its hydrophobicity.

A commonly used measure of tall oil quality is the acid number (AN), which indicates the number of carboxylic acid groups (total fatty and resin acid content). Mills that use only pine have the highest quality CTO, with AN values of 160-165 mg KOH/g oil, whereas mills that use 50% or more hardwood in their furnish have a CTO with an AN of 125-135. Analyses of CTO samples from different parts of the world are presented in Table 1, where the CTO from the south-eastern United States referred to is an example of a very high quality product with pine as the wood furnish, while the Scandinavian example is from a mill using a mixture of pine, spruce and birch. The composition of extractives in hardwoods can have detrimental effects on the quality of CTO end products (Gullichsen & Lindeberg 1999). Many mills in Finland have recently moved towards softwood pulping only, replacing birch pulp with imported eucalyptus pulp, which has improved the quality of their CTO.

Table 1. Composition of CTO (modified from McSweeney et al. 1987).

	South-eastern USA	Northern USA and Canada	Scandinavia		Typical values
			Pine	Pine/ Birch	
Acid number	165	135	150	132	100–175
Saponification number	172	166	169	142	120–180
Rosin acids,%	40	30	31	23	0–70
Abietic acid					
Pimaric acid					
Fatty acids,%	52	55	56	57	20–70
Oleic acid					
Linoleic acid					
Unsaponifiables,%	8	15	13	20	10–30
Sterols					
Waxes					
Hydrocarbons					

4.2 Tall oil as a wood protection agent

4.2.1 *Wood extractives and natural durability*

Wood extractives are known to be the principal source of decay resistance in wood (Scheffer & Cowling 1966), i.e. they act as natural wood preservatives. The use of tall oil as a wood protective agent is interesting because its precursors are the extractives found especially in coniferous trees. Dorado *et al.* 2001, Harju *et al.* 2002, Harju *et al.* 2003, Kennedy *et al.* 1995, Martínez-Iñigo *et al.* 1999, Turner & Conradie 1995, Venäläinen 2002 and Windeisen *et al.* 2001, among others, have investigated the effects of various wood extractives against wood-decaying fungi. Some compounds have a protective effect, whereas others can serve as nutrients for the fungi.

According to Zabel & Morrell (1992), there are four major groups of heartwood extractives that include compounds known or believed to contribute to the natural durability of wood: polyphenols, terpenoids, tropolones and tannins. In the case of Scots pine the relevant groups of extractives are stilbenes and terpenoids (Venäläinen 2002). Pinosylvin (PS), and its derivates pinosylvin monomethylether (PSM) and pinosylvin dimethylether (PSD) represent stilbenes and are typical of the heartwood of *Pinus* species. Venäläinen *et al.* (2003), studying the relationships between decay resistance and chemical and physical wood characteristics found that the most promising characteristics appeared to be the concentrations of pinosylvin (PS) and pinosylvin monomethyl ether (PSM), while Celimene *et al.* (1999) reported that in addition to PS and PSM, pinosylvin dimethylether (PSD), which incidentally can also be isolated from tall oil (Conner 1989), is similarly effective against fungi.

Harju *et al.* (2002) noted that resin acids inherently protect the woody substrate as a result of their toxic effects, and that resin impregnation may act as a non-toxic, waterproofing layer that prevents fungal penetration and growth within wood. It has also been suggested that resin acids may provide resistance against decomposition as a result of their hydrophobic properties rather than their general toxicity (Eberhardt *et al.* 1994). Gref *et al.* (2000) proposed that resin acids play a significant role in decay control in Scots pine wood, but Venäläinen *et al.* (2003) and Harju *et al.* (2002) concluded that, although important for the active defence of living trees, resin acids seem to play only a weak role in passive defence. The active defence mechanisms only occur in the living parts of the tree and involve the formation of toxic chemicals in response to various types of stimulus, such as mechanical wounding, whereas in the passive defence system the components are always in place, e.g. the toxic extractives present in wood (Laks 1991).

The wood extractives that render decay resistance can be complex mixtures with a number of components that have some biocidal activity. Due to this synergistic effect, it may be difficult to determine in which component or components the primary cause of decay resistance lies. Several compounds that are not strong decay retarders individually may occur together in the same wood and contribute greater resistance than the sum of their separate effects (Scheffer and Cowling 1966). The inhibitory effect of resin acids and other fungicidal extractives, however, can be overcome by decay fungi if nutrients such as triglycerides are available in the wood (Gref *et al.* 2000).

4.2.2 Effect of tall oil on the biological durability of wood

Investigations have already been made into the possible use of tall oil as a wood protection agent. Paajanen & Ritschkoff (2002) studied the influence of crude tall oil on the growth of fungi and found it to inhibit the growth of three decay fungi in culture media, the brown rot fungi *Coniophora puteana* and *Poria placenta* and the white rot fungi *Coriolus versicolor*, and a similar effect was found by Alfredsen *et al.* (2004), who screened the potential of certain commercially available refined tall oils with different chemical compositions as potential wood protection agents. Their filter paper assay showed a decrease in growth rate but no total inhibition for any of the tall oils tested. Those with a higher resin acid content were more effective than those with a lower content. Thus efficacy seemed to be dependent on the quantity of resin acids in the tall oil. According to Paajanen & Ritschkoff (2002), tall oil inhibits the growth of brown rot fungi more than that of white rot fungi, but Alfredsen *et al.* (2004) discovered opposite effect. This may reflect the variations in the composition and quality of tall oil mentioned earlier.

The results presented by Alfredsen *et al.* (2004) indicate that Scots pine sapwood treated with tall oil belongs to roughly the same durability class as untreated Scots pine heartwood, between grades 3, slightly durable, and 4, moderately durable (EN 350-1). The investigations of Anon. (1999b), Paajanen *et al.* (1999), Ritschkoff *et al.* (1999) and van Acker *et al.* (1999) indicate a potential for tall oil as a wood protective agent when used in above-ground conditions (EN 335-1/2/3).

Jermer *et al.* (1993) tested the effect of tall oil derivatives against biological degradation, and compared them with preservatives in current use. Their field test showed two tall oil derivatives to be almost equally as effective against decay as CCA and creosote, the retention quantities applied to the wood were extremely high. Terziev (2006) has presented similar results, claiming that stakes treated with crude tall oil at a retention of more than 400 kg/m^3 showed a decay rate of 0 after five years of ground contact, similar to the situation with CCA.

In general, it was expected in the above studies that the efficacy of tall oils against the biological deterioration of wood would be related to the chemical compositions of the oils, but in fact the strongest effect is most probably related to their hydrophobic properties. It is very important, of course, that the impregnant itself does not greatly increase the attraction of decaying organisms to the wood.

4.2.3 Effect of tall oil on water repellency

Treatments with environment-friendly, thoroughly biodegradable tall oil are known to greatly reduce the capillary water uptake of pine sapwood (Anon. 1999b, Paajanen *et al.* 1999, van Eckeveld 2001, van Eckeveld *et al.* 2001a, van Eckeveld *et al.* 2001b). It was noted by van Eckeveld *et al.* (2001b) in their studies of the effects of three tall oils on water repellency that all of them greatly reduced capillary water uptake by the wood, while the results of swelling measurements carried out by Paajanen *et al.* (1999) indicated that crude tall oil treatment has a substantial effect on the dimensional stability of wood. In addition, contact angle measurements showed that impregnation with crude tall oil clearly improve the hydrophobic properties of wood. This was particular evident after ageing in a weather chamber, whereupon a more water-repellent coating had developed on the surface of the wood.

In conclusion, since tall oil treatment reduces capillary water uptake in wood and also imparts hydrophobic properties to the wood surface, water cannot spontaneously penetrate the wood pores through capillary action and the rate of water absorption is limited. This reduces the average moisture content of the wood, and also the period of time for which the wood is wet enough to allow attack by micro-organisms, and thus reduces the risk or rate of fungal attack. This means that tall oil has considerable potential as an alternative wood preservative to those used today.

4.3 Problems related to the use of tall oil for wood protection

Despite the good results, there are two problems that limit the use of tall oil for wood protection: the large amount of oil needed and the tendency for the oil to exude from the wood. Especially when tall oil is used as a biocide, the amount of oil needed to achieve total sapwood penetration is high, and the higher the amount of biocide is, the more effective is the treatment. On the other hand, high retention levels increase the weight of the impregnated wood, and may make it impractical and uneconomic to produce and use. When tall oil is used as a water repellent, however, a smaller amount of oil may suffice as its efficiency is not necessarily dependent on a certain oil retention level.

The tendency for tall oil to exude from the wood arises from the high amounts used and the lack of oxygen inside the wood, which prevents polymerization and oxidation of the oil, causing the unpolymerized oil to exude with time to form a pitch-like surface. This also restricts the applications of wood products treated with tall oil.

4.4 Development of a wood protection process using tall oil

4.4.1 Reducing the amount of oil needed

The problems related to high oil retention levels in the wood can be solved with an appropriate process technique. The retention level can be controlled by changing the process parameters (duration, pressure, temperature) or liquid properties (viscosity, concentration). In Paper II the dilution of the tall oil was chosen as the method of controlling retention, allowing total sapwood penetration to be achieved with smaller amount of oil. For effective treatment, the oil must penetrate through the entire microstructure of the wood, reaching the free surfaces in particular, in order to give it long-term hydrophobic properties. Also, water was used as a thinner instead of the more commonly used organic solvents, on the grounds of environmental concerns, cost and safety. Oil-water emulsions make it possible to use oily water repellents in aqueous situations and to use both water and oil-soluble additives. Furthermore, emulsions are easy to handle (during and after the impregnation process), the surfaces of the products will be cleaner and they will be easier to paint than in the case of wood treated with pure CTO.

The aim of the work reported in Paper II was to investigate the water repellent efficiency of crude tall oil and emulsions containing it, and the possibilities for reducing the amount of oil used by means of the emulsion technique. Scots pine sapwood samples were impregnated with tall oil formulations and the levels of water absorption and degrees of water repellent efficiency (DE) were determined with cyclical wetting and drying tests. High water repellent efficiency means low water uptake by the wood samples (100% means that no change occurred in the specimen, and 0% means that the treated specimen changed as much as the untreated controls). The results support the theory that tall oil treatment reduces the water uptake of pine sapwood, and the tall oil emulsion treatments gave almost as good water repellent efficiencies as pure tall oil, even when the oil retention values were considerably lower (Fig. 18 - 21), showing that the total amount of oil used could be halved. The short-term performance was slightly better in the case of emulsions, and the improvement in long-term performance due to the wetting and drying cycles was higher, although the long-term performance (DE_{96} after six wetting and drying cycles) remained better with CTO. In summary, the emulsion technique was shown to be a potential method for reducing the amount of oil needed to protect wood from water uptake.

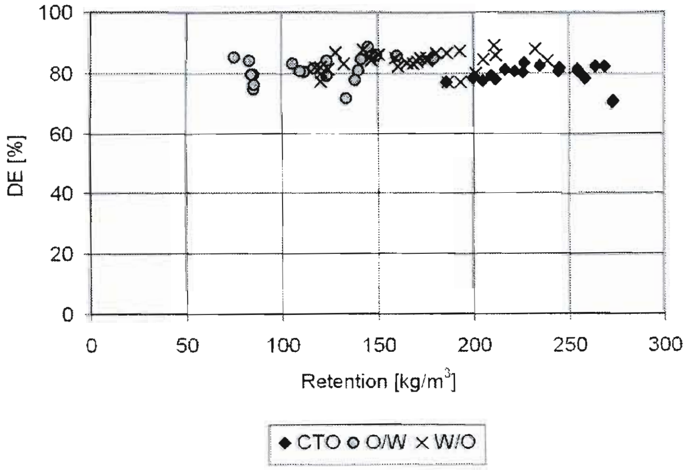

Fig. 18. Degree of efficiency after the initial wetting and drying cycle, measured after 1 hour of water immersion (Paper II).

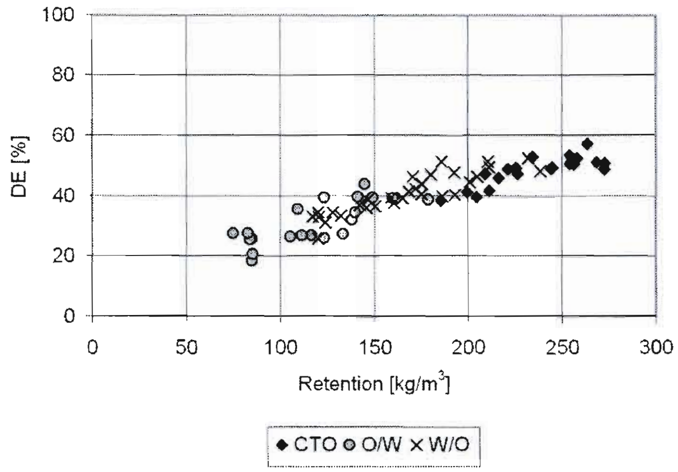

Fig. 19. Degree of efficiency after the initial wetting and drying cycle, measured after 96 hours of water immersion (Paper II).

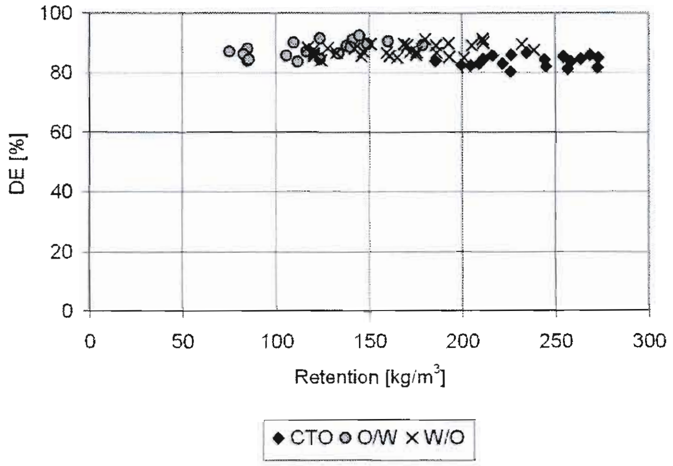

Fig. 20. Degree of efficiency after six wetting and drying cycles, measured after 1 hour of water immersion (Paper II).

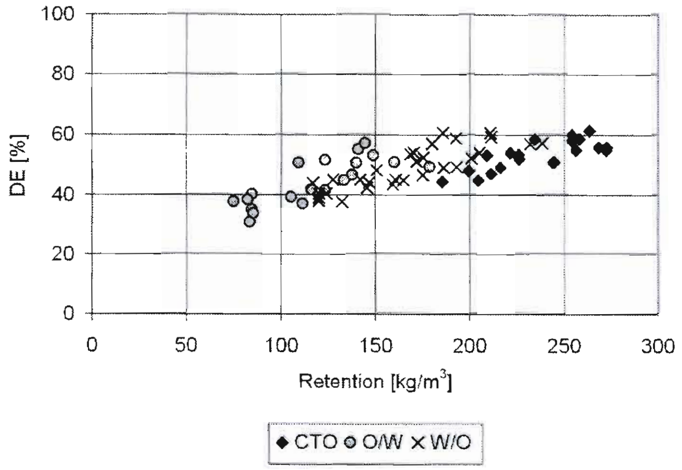

Fig. 21. Degree of efficiency after six wetting and drying cycles, measured after 96 hours of water immersion (Paper II).

4.4.2 Enhancing the drying properties of crude tall oil

The tendency of oil to exude from the wood arises because the lack of oxygen inside the wood prevents polymerization of the tall oil, causing the unpolymerized oil to exude from the wood with time, to form a pitch-like surface. Naturally, the chemical composition of crude tall oil also influences the oil drying process. The problem has been solved by using maleic anhydride to bind the oil within the wood (Paajanen *et al.* 1999), by controlling the ratio of resin to fatty acids in the preservative (WO Patent 03/024680, Carlsson 2003) or by controlling the ratio of carboxylic acids and possibly adding a siccative (FI Patent 97707, Paajanen & Ritschkoff 1997). Under WO Patent 04/022291 the viscosity of the preservative is increased at low temperatures by forming calcium or aluminium soaps of the tall oil fatty and resin acids, so that the preservative solution remains within the wood (Hotanen *et al.* 2004). Neutral agents, unsaponifiables, are also added to the solution to bind the free carboxylic acids as esters. A similar practice is also described in WO patent 03/024681, where calcium and aluminium salts are used to thicken the tall oil and possibly also work as siccatives/catalysts for oxidative cross-linking of the fatty acids in the oil (Johansson 2003). Finally, there is a possibility to achieve a non-tacky surface and reduce the oil exudation problem by decreasing the amount of oil in the surface layers of the wood with an appropriate process technique. However, the obverse is that the water repellency also decreases.

Crude tall oil exudation can be prevented by enhancing its oxidation and polymerization. The work in Paper III was undertaken in order to obtain an understanding of the drying of crude tall oil and methods for improving it, including examining the potential of iron for catalyzing the CTO oxidation process. The drier metals used with oils are usually transition metals M^n ($n = 2\text{-}4$), most commonly cobalt, manganese and zirconium, but iron (Fe^{3+}) can also be used. This offers great benefits when trying to create an environment-friendly, economically viable wood preservative, since iron is non-toxic and much cheaper than the common catalyst metals. It is known, however, that an excess of metal catalyst can cause the reaction rate to slow down (van der Berg 2002), and therefore the optimum amount of iron catalyst needed to be determined. The results proved that the drying properties of pure CTO are too low for it to be used as such in wood preservation, but its oxidation rate can be greatly enhanced by means of iron catalysts (Fig. 22), to the extent that its exudation from the wood can be prevented. As expected, the measurements also indicated that the highest amount of iron does not give the best oxidation result but rather there is an optimum somewhere in between. It should be noted that the composition of the CTO (e.g. the amounts of residual lignin and carboxylic acids present) can vary greatly between mills, and also changes during storage. Thus the amount of iron catalyst determined here was suitable for the particular batch of crude tall oil and may not be the optimum for tall oils from other sources. In practice, the precise amount of iron catalyst should be determined separately for each batch. Instead of qualitative analysis with differential scanning calorimetry (DSC), for instance, this determination can be performed by a simple inclined plane method developed as part of the present research. The results in Paper III enhance our knowledge of the drying process of tall oil-based wood preservative and increase our possibilities for exploiting this substance and other semi-drying oils for wood protection without encountering oil exudation problems.

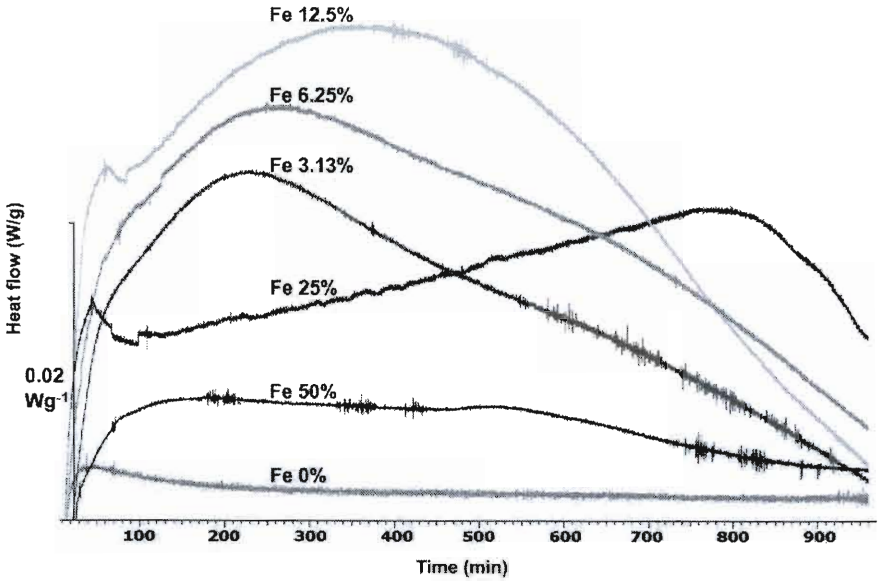

Fig. 22. DSC diagrams (110°C air flow) indicating the oil oxidation rate (Paper III). The higher the curve is, the faster the sample is oxidized.

4.4.3 Enhancing the wood protection properties of tall oil

It would be advantageous from an industrial and economic point of view to be able to solve both problems related to wood protection with crude tall oil in a one single-stage treatment. The studies in Papers IV and V were therefore undertaken in order to improve the possibilities for exploiting tall oil and other semi-drying oils for wood protection without encountering the problems that arise from the high quantities of oil required or its exudation from the wood. The aim was to investigate whether these problems can be solved with one single treatment, i.e. whether it is possible to enhance the drying properties of the emulsion oil phase and also maintain the high water-repellent efficiency. The methods used for enhancing the drying properties were different in the two papers, however.

The water repellent formulations examined in Paper V were based on tall oil fatty acids (TOFA), which are chemically more homogeneous and easier to handle than crude tall oil (CTO). It was assumed that as the dominant physicochemical properties of these oils are alike, they would behave similarly in the various processes and tests. Two of the emulsions were detergent-protected (sodium dodecyl sulphate, SDS) and two polymer-protected (poly(vinyl)alcohol PVA). Iron catalyst was added to one sample of each emulsion. The absorptions, oil retentions and degrees of water repellent efficiency (DE_t) for the tall oil formulae studied in Paper V are shown in Table 2. In spite of the fact that oil retention was higher in the TOFA treatment than in the emulsion treatments, the efficiencies of these treatments are of the same order. The results support the theory presented in Paper II that the emulsion technique is a potential way of reducing the amount of oil needed. As indicated in Table 2, the iron catalyst which accelerates the drying of the oil also improves the water repellent efficiency. van Eckeveld *et al.* (2001b) have reported that continued cross-linking of oil (i.e. drying) during repeated wetting and drying will improve the water repellency of the treatment. In their tests oxidation took place without any catalyst, however. It is suggested in Paper II that acceleration of the drying process by oil modification would also increase its efficiency, and the results presented in Papers IV and V confirm this suggestion. It seems, however, that if the oil is properly dried (solidified) at the beginning of the test, the above improvement in water repellency through oxidative cross-linking of the oil when exposed to air during the wetting and drying cycles will probably not occur. It should be mentioned that untreated control samples normally increase their water uptake during the cycles, but for some reason this did not happen in the present emulsion test series (Paper V), which had a reducing effect on the long-term DE values of the emulsion treatments. Surface-active agents also affect the water repellent efficiency, as shown in Table 2, where PVA are shown to have given higher efficiencies than SDS. It is known that different surface-active agents influence the physical properties of emulsions (e.g. viscosity, particle size distribution) differently, and thereby the penetration and spread of such emulsions within the wood structure.

Table 2. Degree of water repellent efficiency (DE_t) of tall oil-treated pine sapwood samples measured after 1 and 96 hours of water immersion (Modified from Paper V).

Treatment	Absorption	Retention	Degree of efficiency [%]					
			After initial cycle		After four cycles		After six cycles	
			DE_1	DE_{96}	DE_1	DE_{96}	DE_1	DE_{96}
TOFA-SDS	671	255	82	60	73	52	70	49
TOFA-SDS-Fe	623	218	92	64	89	60	89	60
TOFA-PVA	555	223	88	62	88	57	86	54
TOFA-PVA-Fe	603	243	94	67	92	63	92	64
TOFA*	437	386	90	67	91	67	92	70

* Different test series, lower pressure used

The water absorption of the wood samples during the seventh wetting and drying cycle is plotted against the square root of time in Fig. 23. Penetration dominated by diffusion gives a linear curve in this situation (van Eckeveld 2001). Since the capillaries of the wood are more or less closed due to the oil treatment, diffusion-dominated water uptake can be expected. All the treatments except TOFA-SDS show a very clear linear water uptake dominated by diffusion ($R^2>0.99$). The TOFA-SDS emulsion has hydrophilic parts and it is also more generally in a non-solid form than the others. Thus it cannot prevent water uptake by capillarity as well as the other emulsions. The solid oil closes the capillaries more completely than that in a liquid state, and also prevents capillary water uptake in the long term.

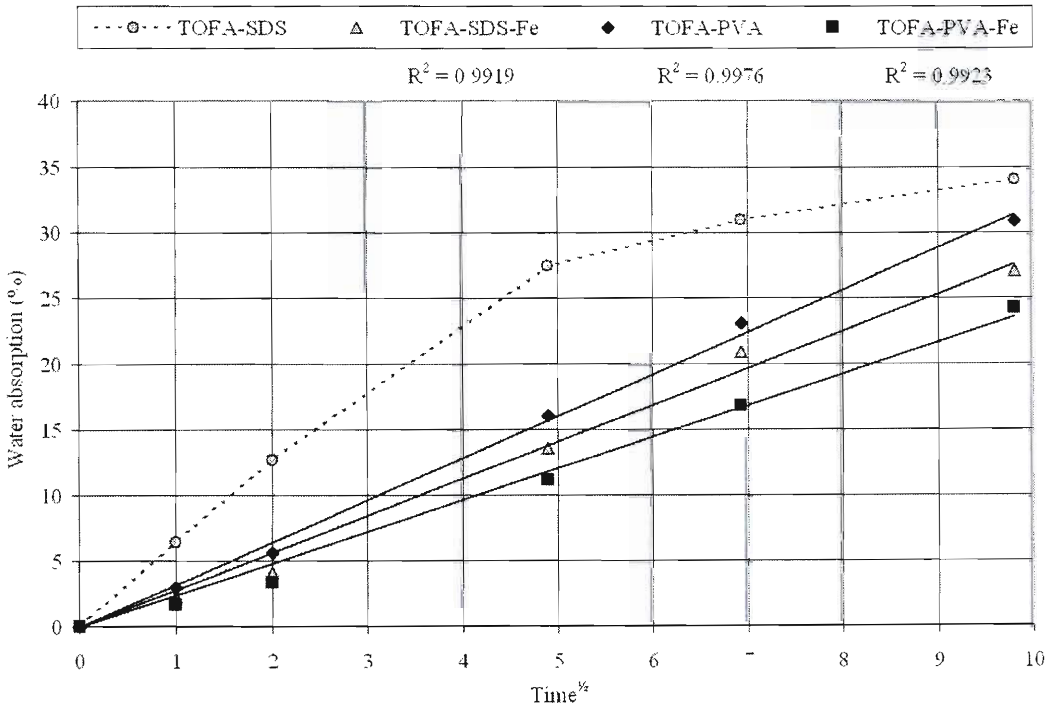

Fig. 23. Water uptake by tall oil-treated pine sapwood in the seventh wetting and drying cycle.

To demonstrate the effect of the iron catalyst on oil drying, this was measured by means of compression tests performed on the treated wood samples. Due to the high degree of oil drying, the pressure needed in the test was higher than that used in previous studies (Sailer 2001, Treu *et al.* 2004). As seen in Fig. 24, the addition of an iron catalyst increases the rate of oil drying and thus reduces the amount of oil squeezed out as a result of compression. Moreover, the use of PVA as a surfactant has an effect in preventing exudation. Probably due to the more uniform penetration, oil drying is better. The decrease in oil pressed out is not a function of the original level of retention (cf. Table 2). Treu *et al.* (2004) note in their discussion of oil drying that when an oil dries a netted hard film is formed. This is an irreversible process. Thus, if any exudation of oil exists, it means that the oil has not dried completely at any stage. The results show that due to the iron addition, the oil within the wood had almost completely dried (less than one percent squeezed out when PVA was used as a surfactant). Most oils do not dry when impregnated into wood in large quantities, however, because the oil hampers the diffusion of air through the wood, which supplies the necessary oxygen. By limiting the oil uptake, a less interrupted air flow can be achieved, and thus the drying process will also be enhanced. Hence both the emulsion technique and the use of an iron catalyst will improve both water repellency and the rate of oil drying. Experience suggests that these same phenomena can be said to occur when treating wood with CTO.

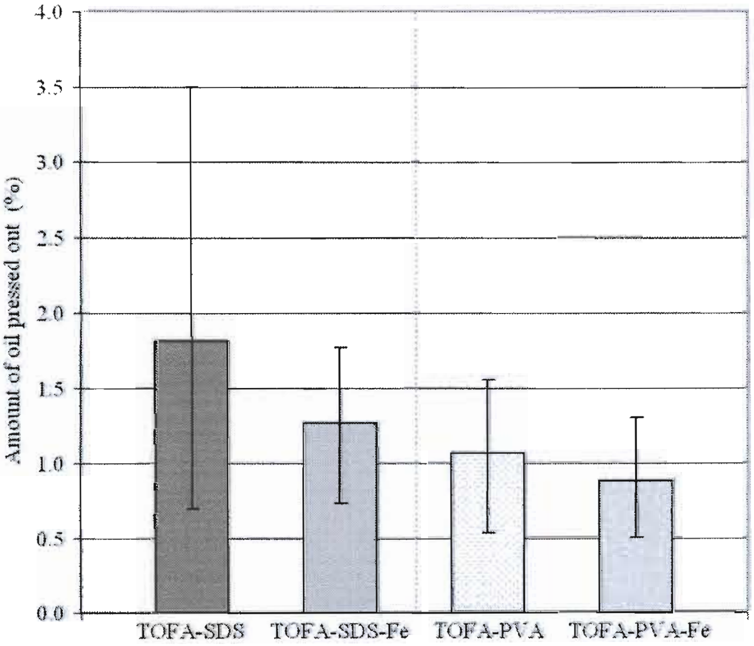

Fig. 24. Amounts of oil pressed out of the samples during the compression test (Paper V).

The results in Paper V show that it is possible to combine the use of an iron catalyst to enhance the drying properties of the oil with the emulsion technique to reduce the amount of oil needed. In addition to enhanced drying properties, the iron catalyst also considerably improved the water repellent efficiency.

In addition to the enhanced drying properties and water repellent efficiencies of tall oil-based wood protection formulations, the emulsion properties are significant as well. The viscosities, average particle sizes and widths of the particle size distributions of the emulsions studied in Paper V are presented in Table 3 and the volume fractions of the particle sizes in Fig. 25. The viscosities of the emulsions were measured with a Brookfield DV II+ Viscometer and the particle size distributions with a Multi-Wavelength Particle Size Analyzer, Beckman Coulter LS 13 320. There were no significant differences in viscosity between the four emulsions, all being in the range 60-85 cP. The viscosity increased on the addition of the iron catalyst, however, when SDS was used as a surface-active agent, and correspondingly decreased in the case of the PVA emulsions. The iron addition increased the average particle size of the emulsions and also widened the particle size distributions and rendered them more uniform. It is good to mention here that iron addition increases the viscosity of pure tall oil, but decreases the viscosity of emulsions.

Table 3. Properties of the tall oil emulsions.

Emulsions	Viscosity (cP)	Average particle size (μm)	Distribution width (μm)
TOFA-SDS	65	1.723	2.894
TOFA-SDS-Fe	85	2.463	7.735
TOFA-PVA	75	1.668	3.144
TOFA-PVA-Fe	60	1.981	5.198

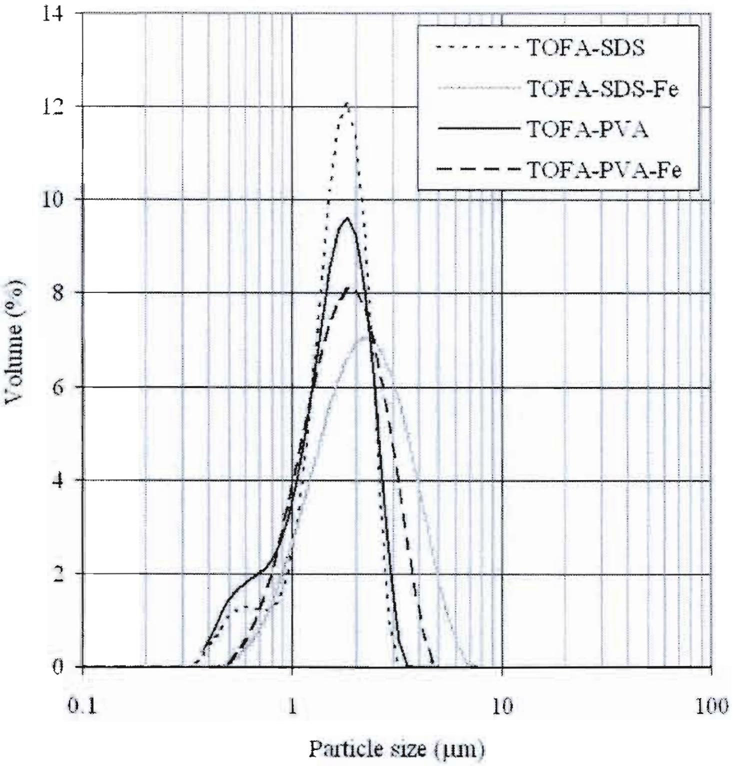

Fig. 25. Typical particle size distribution of a tall oil-based emulsion.

The physical properties, particle size distribution and rheology of emulsions may be at least as important for practical applications as their two-phase structure. Dispersions prepared by mixing or homogenization rarely result in particles of uniform size. Instead, the distribution of particle sizes is heterogeneous, and this has a significant effect on the quality of the emulsion. The aim is usually to produce as small droplets as possible. The size of the particles in an emulsion is a function of the nature of the phases, the quantity and type of surface-active agent and the processing techniques (Bennett *et al.* 1968). Increasing the amount of surfactant in the emulsion and/or the mechanical energy put into the system during preparation will result in a smaller particle size. The resistance to flow, i.e. viscosity, is also one of the most important properties of an emulsion, from both a practical and a theoretical point of view, and the particle size distribution has a great effect on this viscosity. The viscosity of an emulsion increases with a decrease in particle size or in the width of the particle size distribution. (see Becher 2001, Pal 1996, Schramm 1992) In the case of the SDS emulsions used here, however, the iron addition increased both the average particle size and the width of the distribution, but the viscosity of the emulsion increased, although it had been expected to decrease. The reason for this may lie in electrostatic interactions within the emulsion. PVA emulsions are neutral to these, but SDS emulsions are not. The differences in viscosity between these four emulsions did not vary significantly, however. A third important property of an emulsion is its stability. Emulsions have to be stable for a certain period of time, i.e. the droplet size must not increase during storage. An emulsified product loses a great deal of its appeal if it separates into two layers or changes in consistency. Emulsion stability is favoured by a small droplet size and high viscosity. From the point of view of the ultimate use of tall oil emulsions, namely wood preservation, which dictates the properties necessary for an acceptable product (emulsion), there are certain contradictions in this. The primary objective of producing a tall oil emulsion is to obtain a product that can be used in wood preservation, preferably without heating, and stability is a very important factor because it is economically necessary to re-circulate the excess emulsion to the next impregnation batch. A small particle size, which leads to high emulsion stability, is an important factor, too. Particles should be small enough to flow through the wood structure, i.e. the wood cells and their interconnecting pits. In addition, a fairly free-flowing emulsion is desirable. High viscosities, which, as with small particle size, lead to high stability, may cause problems in wood impregnation processes, however. The viscosity of an emulsion should be low enough to provide easy penetration into the wood. Once the emulsion is applied to the wood structure, the oil should easily separate from the water phase due to evaporation, and ideally, it should be deposited deep within the capillary structure of the wood and plug the bordered pits in particular. Thus certain compromises have to be made in order to achieve the optimum composition and properties in an emulsion.

In the case of the emulsions in which SDS was used as the surface-active agent, the retention of tall oil did not correlate with the concentration of the formula, the theoretical tall oil retentions being 40% of the absorption, whereas the actual tall oil retentions attained were on average between 35% and 38% of the absorption (see Table 2). Similar results were achieved in the case of crude tall oil emulsions in which SDS was used as a surface-active agent (Paper II). One explanation for this might be that pine wood acts like a filter for emulsion droplets, as Rapp and Peek (1995) found with water-borne resins. In the case of PVA emulsions, however, the retention of tall oil did correlate exactly with the concentrations. The main routes for liquid penetration into wood are provided by the capillaries, i.e. the lumina of the cells and the interconnecting cell wall openings (pits). When studying the particle size distributions of the emulsions it can be seen that approximately 10% of the TOFA-SDS-Fe particles were of size 4-8 μm (Fig. 25 and Table 3), which might indicate filtration, as the size of the openings of the bordered pits, which are the important limiting factor for liquid flow through the wood, are presumably smaller than this. From the data available, Siau (1971, 1984) stated that the effective radius of the pit openings (openings between microfibrils in the margo) of softwood vary in the range 0.01-4 μm, depending on the species, the condition of the pits and the method of measurement. It should be noted that in some cases the diameter of the pit aperture could be the limiting factor for flow. There are also studies in which the importance of flow through bordered pits is believed to be overestimated, so that there exists (as part of the natural variability in wood microstructure) outer perforation of the pit membrane, which enlarges the flow path (e.g. Olsson 1999). The particle size of a TOFA-SDS emulsion is smaller than that of a TOFA-PVA-Fe emulsion, however, and thus the filtration tendency cannot clearly explain the difference between the actual and theoretical retentions. This brings out another possible explanation, that SDS emulsions are not as stable as PVA emulsions. The SDS emulsion may break up during the pressurized wood impregnation process and/or penetration into the wood, causing higher water penetration than oil penetration. There is also a third possible explanation for the difference between the theoretical and actual retentions. The proportion of retention and absorption of TOFA was 88%, which points to tall oil exudation and/or evaporation during drying of the wood samples. This may also have happened in the case of the SDS emulsions. The reason why the PVA emulsions act differently could be that PVA has film-forming and gluing properties, which hinder the evaporation/exudation of tall oil during the drying stage relative to TOFA and TOFA-SDS emulsions.

In conclusion, it is obvious that certain compromises have to be made in order to achieve the optimum composition and properties in a tall oil emulsion for wood protection purposes. More research is needed in this field, especially concerning the behaviour of tall oil emulsions during the wood impregnation process. For effective treatment, the oil must penetrate through the entire microstructure of the wood, but the filtration mentioned above is not necessarily a negative phenomenon, as it leaves more oil in the surface layers of the wood, which will increases the water repellency of the surface. It should be remembered, however, that water repellency, and thus oil, is also needed deeper within the wood, so that filtration is positive only to a certain degree.

4.4.4 Biodegradability of tall oil-based wood preservatives

Pure groundwater is one of our most important natural resources. In order to protect water sources, it is important to examine the behaviour of possible pollutants in an aqueous environment. Typical wood preservatives such as creosote oil, CCA and PCPs have caused various environmental hazards, and several instances of contamination have been caused by careless use of preservatives and/or location of a wood preservation plant in a groundwater area or close to rivers and lakes (see Lesage & Jackson 1992, Lyytikäinen *et al.* 2001).

The biodegradability of tall oil-based wood harvester hydraulic oils and chain oils has already been studied (Lauhanen *et al.* 2000, Kuokkanen *et al.* 2001, Kuokkanen *et al.* 2004, Vähäoja *et al.* 2005a, Vähäoja *et al.* 2005b), but wood preservation with tall oil is a fairly new application, and research into its environmental aspects is still needed. It was this that aroused our interest in determining the biodegradation of various wood preservatives, mainly tall oil-based ones, in a groundwater environment and under the OECD 301 F standard conditions in water, thus producing more information on their environmental effects (Paper VI). The determinations were carried out by the respirometric BOD OxiTop method, and the results showed that both natural wood preservatives, including tall oil and linseed oil, and the most common raw materials used for tall oil-based wood preservatives were moderately biodegradable in a groundwater environment and that their biodegradation was better under the OECD 301 F standard conditions, where additional amounts of minerals and microbes were present. Notable in the paper VI is that the oxidation of Fe-salt of tall oil fatty acids remarkably decreases the biodegradation rate of oil. This can be seen as an advantage, when tall oil is used for wood protection purpose. The reason to this decrease might be the oil solidification. There were also differences between the biodegradations of certain tall oil fatty and resin acid mixtures and tall oil fatty acid esters, but they were not that significant. Creosote oil, the traditional wood preservative, had no aptitude for biodegradation in groundwater, but some biodegradation ability was shown in the standard tests. Hence, it can be said to be very slowly biodegradable.

4.4.5 Practical applications

The wood protection method presented here enables the two main problems related to wood impregnation with tall oil to be solved in one single-stage treatment which can be implemented at already existing wood preservation plants. This is advantageous from the industrial and economic point of view.

Wood treatment process with crude tall oil emulsion differs from existing processes mainly in preparation of the treatment solution and finishing treatment. It is possible to use commercial emulsions, but in order that the process would be economically and environmentally viable, the excess emulsion and also washing waters should be reusable and/or recyclable. Problem with commercial emulsions is that the properties of emulsion might change during the wood treatment process, and therefore the reusability is difficult. Another problem might arise due to the formation of the washing waters. The finishing treatment, where treated wood and the treatment equipment are washed simultaneously with water, is effective. The excess of emulsion on the wood surfaces can be washed easily out. The washing water can be used in the emulsion preparation process. Therefore, for practical reasons in situ emulsion preparation is recommended, and in that case new emulsification process is needed. However, if stable and easily re-emulsifiable commercial emulsions are available, the process is not needed.

It‘s important to settle the treated wood before oven-drying. This settling time and slow pre-drying in relatively low temperature insure that the evaporating water does not push the oil out of the wood. The drying temperature has an effect of the rate of oil oxidation, and thus the colour of the wood. The higher the drying temperature is the faster is the oil oxidation and the darker is the colour of the wood. The high temperatures (> 100 °C) are not necessarily needed, if the time is not the limiting factor.

The stability of emulsion influences not only the absorption, but also the finishing treatment and the drying behaviour of the treated wood. The finishing treatment of instable emulsion is hard to perform, and there might be oily and pitch-like emulsion residuals on the wood surfaces. Stable emulsion with low viscosity is easier to handle, the impregnated samples and the equipments are much easier to clean, and also, the stability of emulsion oil phase within the wood during drying is higher.

4.5 Considerations concerning tall oil for wood protection

Wood preservation is a way of increasing the biological durability of wood by adding chemicals having a biocidal effect. The effects of such treatments are clearly dependent on the concentrations, so that at specific biocide levels fungi are either killed or their ability to obtain nutrients through their enzymatic functions is inhibited. Non-biocidal treatments act quite differently, however. Mechanisms such as moisture exclusion or hydrophobation retard or prevent colonization by fungi. Since these treatments are only effective above a certain level or when a certain degree of substrate modification is reached (heat treatment), it is seldom possible to establish a dose-response curve (van Acker & Stevens 2000). Thus it is clearly more important to estimate the service life of wood products in different hazard classes than to look for total efficacy. Most non-biocidal treatments are linked to biological hazard class 3 (van Acker & Stevens 2000), where the general service situation is above ground, with exposure to outdoor conditions, and the general moisture level is frequently above 20% (EN 335-1/2/3).

Environment-friendly, thoroughly biodegradable, natural oily substances, including tall oil, are highly suitable for wood protection when the aim is to prevent moisture uptake by the wood. These substances enable the wood moisture content to be kept below 20%, so that the requirements for degradation by fungi are not met. On the other hand, they cannot compete with biocides in terms of the biological durability of wood that is in contact with the ground or water (hazard class 4), where moisture levels in the wood are permanently over 20%.

With the preservatives that were previously in common use, wood can achieve a service life of 50 some years, but the importance of this could be questioned. Even if the life expectancy of an impregnated railway sleeper were 50 years, it might be destroyed by mechanical wear much earlier than this. Creosoted wooden poles become hollow upon ageing, since the biocide-impregnated sapwood is undamaged but the naturally durable heartwood that is difficult to impregnate is totally destroyed. An additional consideration is that wood treated with common preservatives is classified as hazardous waste. Does the life expectancy of garden furniture have to be so long, for instance? Without maintenance, wood will eventually become grey or cracked in any case, and what is more important nowadays, fashions change. Could a 10-year service life be long enough? This would allow timber to be protected with environment-friendly, thoroughly biodegradable substances in order to meet the requirements of various end-use situations and ensure that the treated wood is both “fit for the purpose” and has a useful and safe life cycle, including production, use and eventual disposal.

Both crude tall oil and pine timber are produced in large amounts in Finland. By combining these resources it should be possible to create durable, water-repellent, environment-friendly, biodegradable wood products with good aesthetic properties in this country.

It has been shown that tall oil treatments reduce the water uptake of pine sapwood, and that almost equal water repellent efficiencies can be achieved with tall oil emulsion treatments as with pure tall oil, even at considerably lower rates of oil retention, so that the total amount of oil required could be halved. Thus the emulsion technique is a potential method for reducing the amount of oil needed to protect wood from water uptake. Improved water repellent efficiencies may be connected with increased hydrophobicity of the surfaces and/or the degree of oil drying, but materials such as CTO and TOFA are not usually truly hydrophobic, with a water/solid contact angle of more than 90° (Borgin & Corbett 1970a). Thus the increased hydrophobicity only retards the rate of water uptake in the capillaries. It can be assumed from the results presented in Paper V that the degree of oil drying has an effect on water repellency. Solid oil closes the capillaries more completely than liquid oil and also prevents capillary water uptake in the longer term. It should be noted that treatments with tall oil emulsions above all reduce the rapid water uptake through capillary action that occurs at the beginning of water immersion (high short-term performance). The hydrophobation and closing or filling of the capillaries slows down the rate of water uptake, but the extent of that uptake may still be equal to that of untreated wood over a longer period of time by virtue of diffusion (lower long-term performance). This is a common fact that applies to many other water repellents as well.

As mentioned earlier, most oils do not dry when impregnated into wood in large quantities, because the oil hampers the diffusion of air through the wood, which supplies the necessary oxygen. By limiting the oil uptake using the emulsion technique, a less interrupted air flow can be achieved, and thus the drying process will also be enhanced. Hence both the emulsion technique and the use of an iron catalyst will improve both the water repellency and the rate of oil drying.

According to Razzaque (1982), the effectiveness of a water repellent treatment is probably dependent on both the amount of deposit and its precise location within the treated wood. It is assumed in Paper II that the effectiveness of tall oil emulsion treatment, where the amount of deposit is lower, may be based more on the location of the oil within the wood. Emulsion-treated wood possesses larger amounts of empty space within its structure for liquid water to penetrate than does wood treated with pure CTO or TOFA, where these are filled with oil. The water uptake of emulsion-treated wood might even be lower, however, which would indicate that the routes by which liquid water penetrates the wood were being closed. As the timber dries after treatment, the emulsion breaks up during evaporation of the water and its oil phase is deposited within the inner surface of the lumina, thus plugging the pit membranes and/or increasing the hydrophobicity of the capillary surfaces. Polymerization and drying of the oil during this process greatly increases the efficiency of the treatment. Belford & Nicholson (1969) and Lukowsky (2002), among others, have deduced a similar pit plugging phenomenon, but with different materials.

The main routes for the penetration of liquid into wood are provided by the capillaries; namely the lumina of the cells and the cell wall openings (pits) connecting them. Moisture absorption is very low in the heartwood, since the pits are permanently aspirated (closed), the extractives are deposited on the pit membranes and the pore size is smaller. Sapwood pits also aspirate during drying of the wood, but not permanently. If the tall oil deposit can be positioned on the membranes of aspirated sapwood pits, they remain in an aspirated state due to a "glueing" effect, and water uptake is considerably reduced. According to Lukowsky (2002), it may be assumed that the resin, in this case tall oil, is preferentially deposited in the pit membranes, for as the treated wood dries, the remaining resin solution in the lumen will withdraw to the smallest available capillary, in accordance with the Kelvin equitation, and as the pores of the pit membrane are the smallest capillaries in the lumen, the pits will be plugged by the remaining resin deposits. A notable factor here is that tall oil consists of the same components as heartwood extractives, which are the principal source of decay resistance in the heartwood. It can also be estimated that wood extractives deposited on the pit surfaces may dissolve in an oily impregnant and thus interact with it. Due to this high natural durability and the low moisture absorption rates that make heartwood difficult to impregnate, wood protection is usually aimed at enhancing the durability of sapwood. The use of this method, as presented in Papers I-VI, increases the durability of the sapwood and also makes the wood more homogeneous, while – crucially – allowing the wood to be burned after the end of its useful life. In simple terms, the aim of this method is to turn the sapwood artificially into heartwood.

Thus the field of wood protection has turned full circle since biblical times and the days of Noah's pitched ark …

5 Summary

The research reported here was based on the hypothesis that environment-friendly, biodegradable crude tall oil (CTO) can be used for wood protection and that the related problems can be solved by obeying the rules of green chemistry and engineering. This work was undertaken in order to improve the possibilities for exploiting crude tall oil for industrial wood protection, with the aims of obtaining an understanding of wood protection by means of crude tall oil and finding technical solutions to the main problems limiting its industrial use for this purpose.

The classic approach to wood preservation is based on the principle of toxicity. Wood impregnation with biocides (containing creosote, arsenic, zinc, copper, chromium etc.) prevents biological degradation, but the European directive on the use of biocides place restrictions nowadays on the active substances that can be used in wood preservation, above all arsenic, and their fields of application. Furthermore, wood treated with common preservatives is classified as hazardous waste. Increased environmental awareness in recent years, and the consequent spread of policies favouring the use of renewable resources and environment-friendly chemicals have led to an increased interest in "non-biocidal", more environment-friendly methods of wood protection, even the use of biodegradable substances. Systems enhancing the durability of wood should be sustainable in both production and use. In addition to this, the treated wood products should, at the end of their life, be suitable for energy production by combustion or composting or for use as a secondary fibre source by related industries, without presenting any problems of residual chemicals arising from the treatment.

In addition to toxicity, the prevention of wood degradation can also be based on the idea of interfering in the basic physiological requirements for the growth and development of micro-organisms, including favourable temperatures, an adequate supply of oxygen, at least a certain amount of moisture, suitable nutrition and certain essential growth factors. By changing the circumstances in the wood, e.g. keeping the moisture content below 20%, one can ensure that the requirements for degradation are not met. Controlling the moisture content with water repellents is an effective way of protecting timber. Although water repellents do not stop all water absorption, they are an excellent treatment for wood that is to be used out of doors, because they inhibit the absorption of water at times of rain and yet allow the wood to dry after rain. The reduction in average moisture content and in the length of time for which the wood is wet enough to allow attack by micro-organisms slows down the rate of fungal attack.

Treatments with environment-friendly, biodegradable tall oil are known to reduce the capillary water uptake of pine sapwood greatly, but despite the good results, there are two problems that limit the use of tall oil for wood protection, the large amount of oil needed and the tendency for the oil to exude from the wood. The high retention levels increase the weight of the wood, and may make it impractical and uneconomical to use. It is shown here that the emulsion technique is one way of solving this problem, as it allows high water repelling efficiency to be achieved at considerably lower oil retention levels. In this technique water is used as a thinner instead of the commonly used organic solvents, which is beneficial from the environmental, economic and safety points of view. Oil-water emulsions make it possible to use oily water repellents in aqueous situations and to use both water and oil-soluble additives. Furthermore, emulsions are easy to handle (during and after the impregnation process), the surfaces of the products are cleaner and they are easier to paint than wood treated with pure CTO.

The tendency for oil to exude from the wood arises from the large amounts of oil used and the lack of oxygen inside the wood, which prevents polymerization of the tall oil, causing the unpolymerized oil to exude with time to form a pitch-like surface. This restricts the applications of wood products treated with tall oil. It is shown here that the drying properties of CTO are too low for use as such in wood preservation, but the rate of CTO oxidation and polymerization can be enhanced considerably by means of iron catalysts (Fe^{3+}), thus preventing the oil from exuding out of the wood.

At the same time it is shown that the addition of catalysts to enhance the drying rate of tall oil also increases the water repelling efficiency of tall oil treatment. Most oils do not dry when impregnated into the wood in large quantities, because the oil hinders the diffusion of air through the wood, which brings the needed oxygen. Upon limiting the oil uptake by the means of the emulsion technique the airflow is less disturbed, and thus the drying process is enhanced. Hence, both the emulsion technique and use of an iron catalyst can improve both the water repelling efficiency of tall oil treatment and the rate of oil drying. This method enables the two main problems related to wood impregnation with tall oil to be solved in one single-stage treatment which can be used in already existing wood preservation plants. This is advantageous from the industrial and economic point of view.

Wood can be protected with environment-friendly, biodegradable tall oil in order to meet requirements of various end-use situations, ensuring that the treated wood is “fit for the purpose” and that it has a useful and safe life cycle, including production, use and eventual disposal.

6 Recommendations for future work

The main problems related to wood protection with tall oil, the large amount of oil needed and the tendency for the oil to exude from the wood, have been solved, and the results are promising: tall oil treatment obviously increases the durability and usability of wood. There is therefore real industrial interest in this method. The background to it nevertheless needs to be studied more deeply.

The reason for the increased durability of wood is thought to be the positioning of tall oil droplets in the optimum places within the wood matrix, plugging the sapwood pits and preventing water uptake. It would be important to know how the emulsion droplets flow and position themselves within the wood matrix, and also whether it is possible to contribute to this positioning. The tendency of these substances to be filtered by wood is a highly critical, but not widely known phenomenon, especially in the case of natural oil impregnation, although also in traditional methods. Future studies should concentrate on the effect of process parameters such as pressure, temperature and time, and also emulsion properties such as volume fraction, stability, viscosity and particle size distribution on the penetration and filtration of crude tall oil through the structure of wood, and the localization of the oil within the wood. The possibilities for modelling these phenomena might also be an interesting research topic.

Moreover, crude tall oil can vary considerably in composition and quality, e.g. the amounts of residual lignin and carboxylic acids, depending on the location of the mill, time of year, growing cycle of the tree, tree species, ageing of the wood, amount of heartwood, pulping conditions, handling and storage of the wood, and also in relation to the efficiency of the system used to recover the tall oil. In addition, rosin acids have a tendency to crystallize and settle out from crude tall oil. These variations in composition and quality have a great effect on emulsion formation and behaviour, and also on the amounts of additional chemicals needed. It would therefore be important to find out how the concentrations of different tall oil fractions (resin acids, fatty acids and unsaponifiables) affect the emulsion preparation process and emulsion stability. Threshold values should be determined for concentrations which generate a decrease in emulsion quality.

As mentioned earlier, crude tall oil has an effect on the biological durability of the wood. This results from the chemical composition of crude tall oil. Through oil modification this chemical composition is changed and it can be assumed that this has an effect on the biocidal properties of oil. Therefore decay tests are required. Studying the drying behaviour of treated wood is as important as the wetting behaviour. Also the dimensional changes, cracking, and mechanical properties as well as colour changes, greying, and UV resistance of tall oil-impregnated wood should be studied.

Oil-water emulsions make it possible to use oily water repellents in aqueous situations, and also to use both water and oil-soluble additives. This field is still open for new supplementary research. The combining of crude tall oil treatment and wood cell wall modification with water or oil-soluble substances would be worth studying. Furthermore, an interesting research topic could arise from the possibilities for applying this method to other natural oils, especially semi-drying oils.

In conclusion, despite the fact that the main problems related to wood protection with tall oil can be solved, further investigations are still needed.

Anna Koski References, applicability of crude tall oil for wood protection.

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Attachment 3, section
9

Methods of Analysis for Tall Oil Products

RICHARD HERRLINGER, Arizona Chemical Company, Panama City, Florida

THE TALL OIL INDUSTRY in the United States has grown at a phenomenal rate during the past 10 years. Highly refined products are now being produced from tall oil, such as very light-colored fatty acids, substantially free from rosin acids and rosin substantially free from fatty acids. Manufacturers of paint, varnish, soap, detergents, linoleum, and paper have adopted these products as raw materials and depend on their quality and uniformity. It is therefore not surprising that, in the United States, considerable attention has been given to, and a lot of work has been done on the development of suitable methods of analysis for these products.

Most of this work was carried out in laboratories of producers and users of tall oil products in collaborative tests under the auspices of the American Society for Testing Materials (Committee D-17) with the support of the Tall Oil Division of the Pulp Chemical Association. Some methods developed by committees of the American Oil Chemists' Society for the analysis of fatty acids have also found application for tall oil fatty acids. It is the purpose of this paper to give a short review of some of the A.S.T.M. work and to discuss present methods for the analysis of tall oil products in general.

Tall Oil and Tall Oil Fatty Acids

Analytical values which are often or occasionally determined on crude tall oil, acid-refined tall oil, distilled tall oil, and tall oil fatty acids are as follows:

Chemical Values. Acid number, saponification number, rosin acids, fatty acids, unsaponifiables, polyunsaturated fatty acids (conjugated and total linoleic acid), saturated fatty acids, oleic acid, and iodine value.

Physical Values. Color, moisture, specific gravity, refractive index, viscosity, flash point, pour-point, cloud-point, and titer.

Values for typical tall oil products in the United States are given in Table I.

. Acid values and saponification values are determined according to the time-honored methods of the oil and fat chemists. Methanol is universally used as a solvent and methanolic KOH as titrant. While potentiometric titration is specified in the referee methods of the A.S.T.M., the use of thymol blue or phenolphthalein as indicator is popular in many laboratories because of speed or convenience.

The determination of rosin acids is more complicated and has a long history of development. The first to solve this problem was Twitchell (1). By bubbling hydrochloric acid gas through solutions of rosin and fatty acids in alcohol, he made use of their different esterification rates and was able to convert the fatty acids into their respective esters while the rosin remained unesterified and could be titrated. This principle of selective esterification is still the basis of all present methods, which in the meantime have undergone many changes to make them simpler and faster. Wolff (2) in 1910 introduced the use of sulfuric acid as an esterification catalyst. There were a number of investigations in Germany, Sweden, and the U.S.A., which contributed to methods of rosin acids determination. While in Europe the slower gravimetric methods, in which the fatty acid esters are isolated and weighed, became standards of the industry; in the U. S. emphasis was placed on simple manipulation and speed. A simple and fast modification of the Wolff method was developed by Hastings and Pollak and published in 1939 (3). It consisted in refluxing a sample of tall oil in methanol in the presence of sulfuric acid for 2 min., cooling, and titrating the unesterified rosin acids by using a thymol blue indicator. This indicator, because of its two color changes, allows measurement of the rosin acid aside from the mineral acid in one titration. The A.S.T.M. adopted this method and added potentiometric titration, which eliminates difficulties in determining the end-points, particularly in such dark-colored products as crude tall oil (4).

The McNicoll method (5), which uses naphthalene sulfonic acid as a catalyst and titrates unesterified rosin acids with phenolphthalein as indicator against a blank was first employed for the determination of rosin in soap. It too became an A.S.T.M. method for tall oil.

By 1953 experience in our own laboratory and investigations by Sprengling (6) and Hezel (7) indicated that the reflux time of 2 min. for the Wolff Method was too short. We decided to determine the reflux times necessary for rosin acid mixtures of 30 to 50%, corresponding to the crude and refined tall oil products of commerce. The mixtures were prepared from rosin-free distilled soybean fatty acids and from tall oil rosin acids repeatedly recrystallized from methanol. A Beckman Model K automatic titrator was used. To determine the end-points which would give the most accurate results in connection with automatic titrators, potentiometric titration curves were first plotted with 10 different commercial crude tall oils, four distilled tall oils, and two acid-

TABLE I
Analysis Values of Typical U. S. Tall Oil Products

Product	Acid No.	Sap. No.	Rosin acids	Unsap.	Fatty acids	Color, Gardner	Specific gravity 25°/25°C.	Refractive index 25°C.
Crude tall oil			%	%	%			
Low rosin	170	174	40.0	6.9	52.5	17	0.980	1.5030
High rosin	166	172	49.0	7.1	43.1	18	0.975	1.5100
Distilled tall oil	190	194	29.0	1.2	69.8	7+	0.947	1.4860
Acid refined tall oil	169	173	40.0	6.8	53.1	8	0.980	1.5025
Tall oil fatty acids	192	194	4.0	4.0	92.0	7+	0.901	1.4719
	196	197	1.2	1.5	97.2	5+	0.900	1.4670
	198	199	0.4	0.4	99.2	3	0.897	1.4645
Tall oil heads	172	177	0.5	15	84.4	12+	0.905	1.4754
Tall oil rosin	168	176	94[a]	4.0	2.0	WW[b]	1.060	—
Tall oil pitch	55	115	32	32	30	17[c]	1.005	—

[a] Includes rosin esters and anhydrides. [b] U. S. rosin color standards. [c] 10% solution in benzene.

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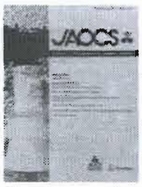

Methods of analysis for tall oil products

Journal	Journal of the American Oil Chemists' Society
Publisher	Springer Berlin / Heidelberg
ISSN	0003-021X (Print) 1558-9331 (Online)
Issue	Volume 36, Number 3 / March, 1959
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Subject Collection	Chemistry and Materials Science
SpringerLink Date	Friday, June 01, 2007

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Richard Herrlinger[1]

(1) Arizona Chemical Company, Panama City, Florida

Summary The principal standard methods used by the American industry for the analysis and quality control of tall oil products have been discussed, and some of the work of the A.S.T.M. in developing these methods has been reviewed.
Further growth of the tall oil industry will undoubtedly result in new products of greater refinement and wider utilization. New and improved methods of analysis will be required. These can be worked out by the industry in continued collaborative work under the auspices of the A.S.T.M. and A.O.C.S. Undoubtedly instrumental test methods such as infrared and ultraviolet spectroscopy and gas chromatography will play a role of increasing importance in the analysis of tall oil products.

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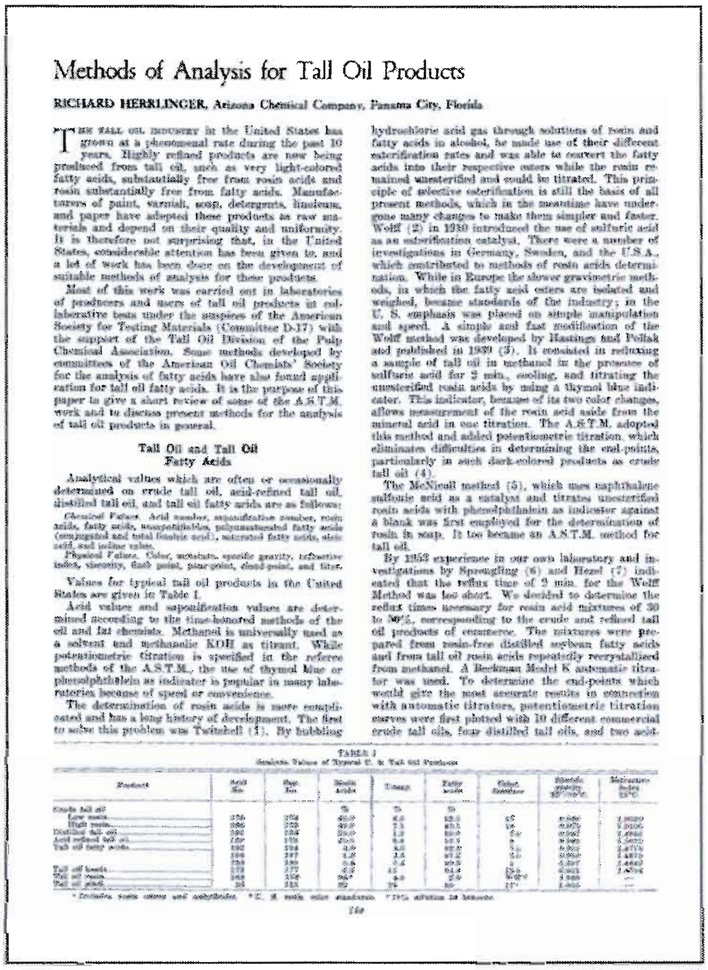

Methods of Analysis for Tall Oil Products

RICHARD HERRLINGER, Arizona Chemical Company, Panama City, Florida

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TABLE I

References secured to subscribers.

Attachment 4, section: 9
Reference - Dydahl
AR 201- 13056 B

IV. Robust Summaries of Existing Data

PHYSICO-CHEMICAL PROPERTY – OCTANOL/WATER PARTITION COEFFICIENT	
Test Substance	
Chemical Name	Tall oil
CAS #	8002-26-4
Remarks	This substance is referred to as tall oil in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Testing was conducted according to OECD Test Method 117, "Partition Coefficient (n-Octanol/Water) High Performance Liquid Chromatograph (HPLC) Method"
Test Type	Partition coefficient
GLP (Y/N)	Y
Year (Study Performed)	1993
Test conditions	Tall oil was dissolved in methanol and the solution was analyzed by HPLC with UV detection using a mobile phase of methanol:buffer (3:1) at pH 2 and pH 7.5. As a reference substance, a mixture of seven materials was used.
Results	At pH 2, the log P_{ow} [K_{ow}] values of eight components in tall oil were 6.1, 6.5, 7.0, 7.4, 7.6, 7.8, 8.1, and 8.2. At pH 7.5, the log K_{ow} values of five components in tall oil were 3.5, 4.2, 4.5, 4.7, and 5.4.
Data Quality	Reliable without restrictions – Klimisch Code 1a Note: the various K_{ow} values reflect the components in the mixture and not the mixture *per se.*
References	Dybdahl, H.P. 1993. Determination of log P_{ow} for single components in distilled tall oil. GLP Study No. 408335/475. Water Quality Institute, Horshølm, Denmark.

Attachment 5, section 9

☒	**SAFETY DATA SHEET** According the directive 91/155/ETY

forchem

Date: 10.11.2008 **Former date:** 17.08.2006

1. IDENTIFICATION OF THE CHEMICAL AND OF THE MANUFACTURER, IMPORTER OR OTHER UNDERTAKING

1.1 Identification of the substance or preparation

Trade name **Distilled Tall Oil**
X-Qualities
FOR 20X, FOR 20/25X
FOR 25/30X, FOR 30/40X

1.2 Use of the chemical

1.2.1 **The intended uses of the chemical**

1.2.2 **Standard industrial classification (SIC)**

1.2.3 **Use categories (UC62)**

1.2.4 **The chemical can be used by the general public** ☐

DEC 15 2008

1.2.5 **The chemical is used by the general public only** ☐

1.3 Identification of the manufacturer, importer or other undertaking

1.3.1 **Manufacturer, importer, other undertaking** Forchem Oy

1.3.2 **Contact information:**

Street address	Maanpääntie 3
Postcode and post office	26100 Rauma, Finland
Post-office box	P.O.Box 16
Postcode and post office	FIN-26101 Rauma, Finland
Telephone number	+358-2-4784 400
Telefax	+358-2-4784 499
Y code	1614382-3

1.3.3 **Information on foreign manufacturer**

1.4 Emergency telephone

1.4.1 **Telephone number, name and address**
+358 50 3104413 , Mikko Rintola Quality Manager, Forchem Oy Finland

2. COMPOSITION AND INFORMATION ON INGREDIENTS

2.1 Hazardous ingredients

2.1.1 CAS number or other code	2.1.2 Name of the ingredient	2.1.3 Concentration	2.1.4 Warning symbol, R phrases and other data on the ingredient
8002-26-4	Distilled tall oil	100 %	None

2.1.5 **There has been a request for confidentiality of a substance according to Annex 3 of the decree** ☐

DEC 15 2008

2.1.6 **A substance not dangerous has been indicated as confidential** ☐

2.1.7 **Other information**
EINECS NUMBER: 232-304-6

3. HAZARDS IDENTIFICATION

Product is yellowish oily liquid with a vegetable oil odour. Product is not considered to be combustible. Except after prolonged contact with highly porous materials.

- Over exposure:	Might irritate eyes
- Exposure to skin:	Might irritate slightlly
- Contact with eyes	Possible irritation

4. FIRST AID MEASURES

4.1 Special instructions

4.2 Inhalation

Move person to non-contaminated air, if person is not breathing, apply artificial respiration, seek medical attention.

4.3 Skin contact

Wash with soap and water. If hot product contacts skin, cool under running water and get medical attention.

4.4 Eye contact

Rinse immediately with plenty of water and get medical attention. If hot product contacts eye, flush with water and get medical attention immediately.

4.5 Ingestion

Rinse mouth with water

4.6 Information to doctor or other trained persons giving first aid

5. FIRE-FIGHTING MEASURES

5.1 Suitable extinguishing media

Powder, carbon dioxide, foam, watermist (only large amounts).

5.2 Extinguishing media which must not be used for safety reasons

Not applicable

5.3 Special exposure hazards in a fire

In case of fire toxic fumes might be formed.

5.4 Special protective equipment for fire-fighters

Wear protective clothing and use self-contained breathing apparatus

5.5 Other instructions

6. ACCIDENTAL RELEASE MEASURES

6.1 Personal precautions

Put on adequate protective equipment.

6.2 Environmental precautions

Keep away from drains, surface-water, ground-water, and soil.

6.3 Methods for cleaning up

Collect as much as possible in a clean container for disposal. Cover the remainder with inert absorbent. Disposal according to local regulations.

6.4 Other instructions

7. HANDLING AND STORAGE

7.1 Handling

Avoid contact with eyes.

7.2 Storage

Direct sunshine should be avoided. Warm product can self-ignite when soaked into porous material.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Exposure limit values

8.1.1 HTP values

Not applicable

8.1.2 Other limit values

Not applicable

8.1.3 Limit values in other countries

Not applicable

8.2 Exposure controls

8.2.1 Occupational exposure controls

8.2.1.1 Respiratory protection

Suitable respiratory equipment.

8.2.1.2 Hand protection

Protective gloves.

Material of gloves

(PVC or PE gloves)

The choice of the suitable glove is not only dependent on the material but also on other quality issues and differs from manufacturer to manufacturer

Penetration time of glove material
The exact break trough time has to be found out by the manufacturer of the protective gloves and has to be observed.

8.2.1.3 **Eye protection**
Safety goggles.

8.2.1.4 **Skin protection**
Suitable protective clothing.

8.2.2 **Environmental exposure controls**
N/A

9. PHYSICAL AND CHEMICAL PROPERTIES

9.1 **General information (physical state, colour and odour)**
Liquid,yellow, faint odour.

9.2 Important health, safety and environmental information

9.2.1 **pH**
Not applicable

9.2.2 **Boiling point/boiling range**
>200 °C

9.2.3 **Flash point**
200 °C

9.2.4 Explosive properties

9.2.4.1 **Lower explosive limit**
None

9.2.4.2 **Upper explosive limit**
None

9.2.5 **Oxidising properties**
Not applicable

9.2.6 **Vapour pressure**
Not known

9.2.7 **Relative density**
0.930 (20 ° C) (=Density 930 kg/m^3)

9.2.8 Solubility

9.2.8.1 **Water solubility**
Not soluble

9.2.8.2 **Fat solubility**
Soluble

9.2.9 **Partition coefficient: n-octanol/water**
$\mathrm{Log}_{10}P_{ow}$ 3.5 - 8.2

9.2.10 **Viscosity**
80 mPa s (20° C) (= 80 cP)

9.3 **Other information**
-

10. STABILITY AND REACTIVITY

10.1 **Conditions to avoid**
Excessive heating with porous material.

10.2 **Materials to avoid**
Porous material

10.3 **Hazardous decomposition products**
N/A

11. TOXICOLOGICAL INFORMATION

11.1 **Acute toxicity**
None

11.2 **Irritation and corrosiveness**
Eye contact: Irritating

11.3 Other information on health effects
Ingestion: Oleic acid: LD50, oral-rat=74 g/kg. Linoleic acid:LD50, oral-rat>3,2 g/kg.
Resin acid: LD50 oral-rat 7,6 g/kg; LD50 oral-mouse 4,6 g/kg.

12. ECOLOGICAL INFORMATION

12.1 Ecotoxicity

12.1.1 Aquatic toxicity
Water Hazard Class (Wassergefährdungsklasse) 2
Fish LL$_{50}$ (96h) > 10 000 mg/l WAF (OECD 203)
Daphnia EL$_{50}$ (48h) > 10 000 mg/l WAF (OECD 202)
Algae EL$_{50}$ (72h) > 1000 mg/l WAF (OECD 201)

12.1.2 Toxicity to other organisms
NOEC > 1000 mg/l, Bacteria E$_{50}$ > 10 000 mg/l WAF (ISO 10712). NOEC > 10 000 mg/l

12.2 Mobility
Not applicable

12.3 Persistence and degradability

12.3.1 Biodegradation
73 % 28 days (OECD 301F)

12.3.2 Chemical degradation
Not applicable

12.4 Bioaccumulative potential
Not applicable

12.5 Other adverse effects
Not applicable

13. DISPOSAL CONSIDERATIONS

Method of disposal: Controlled incineration.
Danger(s): Warm product can self-ignite when soaked into porous material.

14. TRANSPORT INFORMATION

14.1 UN number
Not classified

14.2 Packing group

14.3 Land transport

14.3.1 Transport class
Not classified

14.3.2 Risk code
Not Classified

14.4 Sea transport

14.4.1 IMDG class
Not classified

14.4.2 Correct technical name

14.4.3 Other information

14.5 Air transport

14.5.1 ICAO/IATA class
Not classified

14.5.2 Correct technical name

14.5.3 Other information

15. REGULATORY INFORMATION

15.1 Information on the warning label

15.1.1 Letter code of the warning symbol and indications of danger for the preparation
Not classified

15.1.2 Names of the ingredients given on the warning label
N/A

15.1.3 R phrases
None

15.1.4 S phrases

None

15.1.5 Special regulations on certain preparations

N/A

15.2 National regulations

N/A

16. OTHER INFORMATION

16.1 List of the relevant R phrases

None

16.2 Training advice

16.3 Restrictions on use

None

16.4 Further information

Forchem Oy, Finland
P.O.Box 16
FIN-26101 Rauma

Mikko Rintola
Quality Manager
tel.+358 2 4784 413

16.5 Sources of key data used

16.6 Information which has been added, deleted or revised

Attachment 6, Section 9

DEC 15 2008

Naval Stores Research at the Forest Products Laboratory, Past and Present

Naval Stores Review 97(1):5-8 (1987).

By Duane F. Zinkel
Forest Products Laboratory, Forest Service, U.S. Dept. of Agriculture
One Gifford Pinchot Drive, Madison, WI 53705-2398

Presented at the 13th International Naval Stores Meeting.
New York, September 16, 1986.

As many of you may not be familiar with Forest Products Laboratory, allow me to introduce it to you. The Forest Products Laboratory is a Federal government laboratory of the United States Department of Agriculture and, more specifically, of the Forest Service. The Laboratory was built in Madison, Wisconsin in close cooperation with the University of Wisconsin to serve as the national center for wood utilization research.

The broad mission of Forest Products Laboratory is "to improve utilization of wood through research that leads to improved management of the timber resource, thus meeting the needs of the United States and contributing to the international community." Utilization research at the Laboratory covers eleven program areas:

Program Area	**Number of Scientists and Other Technical Professionals**
Material Properties and Construction	18
Pulp and Paper	17
Preservation and Protection	13
Composite Products and Adhesives	12
Biological Conversion Processes	9
Timber Requirements and Economics	9
Solid Wood Processing	8
Mycology	5
Chemicals and Energy	4
Anatomy and Wood Identification	3
Packaging	2

An overview of the broad range of past and present research at FPL is found in the Laboratory's 75th Anniversary publication, "Age of Wood: Progress through Wood Research," available from Publications Distribution at the Laboratory.

Past Naval Stores Research at FPL

Research related to naval stores began in the Forest Service at the turn of the century, several years before establishment of the Forest Products Laboratory.[+] This early work was done as a cooperative effort with the Bureau of Chemistry's dendro-chemistry laboratory. At the same time, Charles Herty began a study on gum oleoresin methodology which led to the development of the cup and gutter system. Naval stores research at the Forest Products Laboratory in Madison actually began before construction of the original laboratory facility was completed in 1910. C. F. Hawley used the University of Wisconsin's heating plant for conducting research to improve the odor characteristics of wood turpentine. Research by Hawley and his colleagues on wood distillation products and on the basic chemistry of pine extractives continued over the next two decades. But by the end of that period, wood distillation was being de-emphasized. In the early 1920's, Dr. Eloise Gerry, a botanist by mining, began a thorough study on tapping methods. This work culminated in the 1935 publication of "A Naval Stores Handbook Dealing with the Production of Pine Gum or Oleoresin." During the following 25 years, naval stores research was at a low ebb with only a few studies being done in this area.

Present Naval Stores Research at FPL

The present period of FPL research in naval stores began in 1961 as a cooperative program between the Laboratory and the Pulp Chemicals Association. In general, the research effort has been at a modest level by a few senior scientists but it has been a continuing effort.

This research program has had a fundamental direction that is well-embodied in the objective statement "to improve the recovery and utilization of talk oil and related materials through a better understanding of the chemistry." To achieve this "better understanding of the chemistry," we emphasize basic research. Although tall oil and pulping byproducts are explicit in the objective statement, the relation to other sources of naval stores is equally implicit.

Based on our research experiences and on research needs, we have categorized the research efforts into three areas to indicate the primary thrust of the research. They are: Analytical development, Chemistry of recovery, and Chemistry of components. None of the areas is exclusive; most any study will have elements of all three.

Analytical Development—Our studies of analytical methodology have taken several directions. One of the major directions is in the gas chromatographic determination of the resin acid composition of rosins, oleoresins and extractives. Over the years, the analysis was accomplished with packed columns (still the current ATSM method) but most recently is done with glass or fused silica capillary columns. Gas chromatography is one of our most powerful tools in the overall spectrum of naval stores research.

[+] C. A Nelson, "History of the U.S. Forest Products Laboratory (1910-1963)." Forest Products Laboratory, Madison, WI. (1971).

Whereas gas chromatography is most useful in detection and tentative identification of components, modem spectrochemical methods, such as nuclear magnetic resonance and mass spectroscopy, are critical in definitive characterizations of components. In the early years of my research, I purified a large number of resin acids in order to develop a reference file of spectra. However, I realized that for many of the resin acids, our 25 mg represented the world's supply of pure material. This led to sharing our spectral data in the form of a published compilation, "Diterpene Resin Acids-A compilation of infrared mass, nuclear magnetic resonance, ultraviolet spectra and gas chromatographic retention data." The compilation is extensively used in industrial, government, and academic laboratories.

In related work, we have developed a variety of analytical and separation methods such as:

DEAE-Sephadex for quantitative separation of acids and neutrals

Gel-permeation chromatography for separation of fatty from resin acids

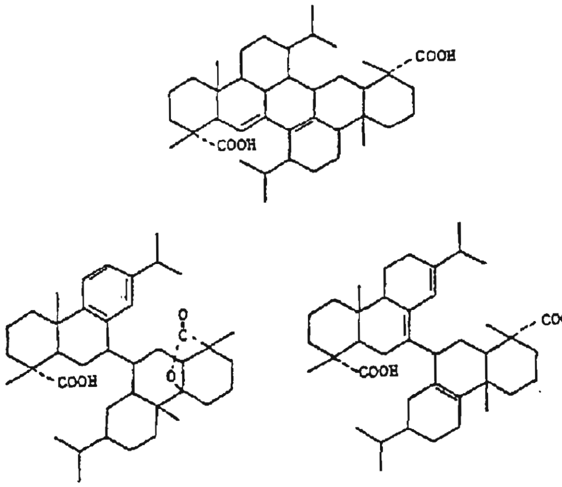
Argentative (silver complex) chromatography for the isolation of individual components

Currently, we are attempting to develop a rapid method for tall oil content in black liquor to replace the reliable, but time consuming, Buckeye method. In the future, we envision the development of naval stores analytical methods based on supercritical and countercurrent chromatography.

Chemistry of Recovery—The discovery of induced lightwood formation in the mid-1970s led to our most extensive single effort in naval stores research. The effort was 4-5 years in duration involving as many as five senior FPL scientists from several disciplines. Most of this work, as you would expect, was in cooperation with the Southeast Forest Experiment Station at Olustee, Florida. This work included the chemistry of lightwood extractives, the extent of lightwood production in a variety of conifers, the pulping of lightwood, and the physiology of lightwood formation.

Another area of extensive FPL involvement has been on the effect of storage of pulpwood chips on byproduct recovery. Of the preservative treatments that were investigated, the chemical N-methyldithiocarbamate (well known under the trade name of Vapam) was the most promising. Although the current economics of chip treatment are marginal, the research work led to the formulation by Dr. Edward Springer of chip-storage strategies for better naval stores recovery and better pulp yield. A publication on standby storage by Dr. Springer is a landmark in this area.

FIGURE 1. Three known types of resin acid dimers.



In other research on tall oil recovery, we demonstrated by use of radiochemical (carbon-14) labelling and by rigorous analytical work that the fatty acids and resin acids comprising tall can be completely recovered from pulping. But one of the major problems hindering the recovery is the absorption of the fatty acid/resin acid soaps on the pulp.

In my earlier synopsis of the history of naval stores research at FPL, I noted that the Laboratory was extensively involved in gum naval stores research. Although much of our current Chemistry of Recovery research is pulping byproduct oriented, we have been specifically involved in gum research. Most recently, we collaborated on a study with our Olustee Forest Service compatriots on the efficacy of ethylene/sulfuric acid stimulation of oleoresin flow and composition. In the course of this work, we isolated several resin acids new to those previously known to occur in slash and longleaf pines.

Chemistry of Components—I noted at the onset of this discussion of current FPL research that the three general categories are overlapping. The initial direction of an investigation of pine foliage was as a new source of naval stores chemicals and. as such. fits into the category of Chemistry of Recovery. However, the major thrust soon became the isolation and identification of a host of new diterpene resin acids. that is, an investigation of the chemistry of components. Although resin acids of pine foliage have a potential as a source of fine chemicals. the most immediate application is in insect feedant studies and in chemotaxonomy. Any further effort now in this area is of low priority. However, we have defined the opportunities in resin acid-foliage research and have devised some of the necessary analytical methodology to conduct the research.

Rosin dimers are commercially important derivatives of rosin; but until recently, little was known about the chemical structures involved. Our study of the dimerization reaction shows that several general types of dimer components are involved (Figure 1). Their chemical structures suggests that a variety of products having different characteristics can be prepared. In some related work involving the preparation of rosin polyesters as models for dimer analytical methods, we discovered a new reaction for preparing rosin ester. Of particular note is that certain esters, not possible from other methods, can be prepared.

In another study nearing completion, we investigated the composition of U.S. distilled tall oils. In the course of this work, we identified a previously unknown resin acid, the pimaric acid double bond analog of isopimaric acid, i.e., 7,15-pimaradien-l8-oic acid.

This brings me to the Texas Snow Job — a most unusual story of naval stores utilization. The Texas Snow Job, a development of the Texas Forest Service. is a method for fighting brush fires and fires in small wooded areas that uses dilute solutions of tall oil soap skimmings to produce a stable, fire-smothering foam. After the fire, the coating of foam on brush and trees has the appearance of a recent snowfall, hence the "Snow Job" name. Our contribution was in providing background information on the chemistry of soaps, chemical analysis, and in providing advice during later testing by the U.S.D.A. Forest Service.

Summary and Final Comments

In this limited time, I have provided a brief review of the naval stores program at the Forest Products Laboratory. An indication of the range of this research is reflected in a selection of publications listed at the end of this paper. (A complete list of FPL naval stores-related publications can be obtained from the author.)

The naval stores research program at the Forest Products Laboratory has a long and invaluable association with the Pulp Chemicals Association. The recent study on American distilled tall oils, for example, was a result of a PCA fellowship for a gifted young chemist. As a direct result of the FPL-PCA cooperation over the years, further cooperation has taken place with PCA member companies and their scientists, resulting in a number of publications. Other cooperative research involves other Forest Service and government laboratories, universities and colleges, and with visiting scientists and Post-doctoral fellows from the United States and overseas.

One facet of the PCA-FPL cooperation is an annual review of the research program at FPL. A recurring item of discussion is how can we maintain and improve our FPL naval stores program (particularly in these times of tightening budgets) and how can we at FPL effectively share the knowledge and expertise that we have developed over the years, beyond that achieved in our publications. Three feasible options are:

1. Visiting scientists at FPL from industry (sabbaticals)
2. Support of students at FPL; this could include summer opportunities, work-study programs, graduate and undergraduate research (thesis), and special scholarship/work-study programs at minority colleges and universities.
3. Special situations of supported cooperative research. This could include continuing research from 1 (above), three-way FPL-academic-company programs, or post-doctoral fellowships.

Some of these options have been put into practice. Working with me have been two industry scientists from Japan (for 1 year each); a post-doctoral scholar from France; short-term visiting scientists from Portugal, the Peoples Republic of China, and Mexico; and a number of graduate and undergraduate students. We plan to continue this program. I will be glad to discuss further such options for cooperative naval stores research. You can write to me at the Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53705-2398; or telephone (608) 264-5857. o

SOME PUBLICATIONS OF THE FOREST PRODUCTS LABORATORY

Conifer Extractives, Naval Stores, and Tall Oil

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Rousseau, R.W., Kassebi, A., and Zinkel, D.F. Effects of solids content, settling temperature, and liquor source on tall oil solubilities. AIChE Symp. Ser. 239. 80:1-8 (1984).

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Burgstahler, A.W., Marx, J.N., and Zinkel, D.F. Structure and sterochemistry of reduction products of abietic-type resin acids. J. Org. Chem. 34:1550-1561 (1969).

Zinkel, D.F., Rowe, J.W., Zank, L.C., Gaddie, D.W., and Ruckel, E.R. Unusual resin acids in tall oil. J. Amer. Oil Chem. Soc. 46:633-634 (1969).

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Attachment 7, section 9

Tall Oil

Lars-Hugo Norlin, Bergvik Kemi, Sandarne, Sweden

DEC 15 2008

1. Introduction

"Tall" is the Swedish word for pine, and the term tall oil is an American adaptation of "tallolja," a Swedish product name associated with the kraft pulping process (→ Paper and Pulp, Chap. 1.3.1.1.) and with products from the fractional distillation of crude tall oil.

Pine wood contains an extractable fraction, ≈ 3 %, consisting of free and combined fatty and rosin acids and nonacidic compounds (tall oil components). In the alkaline pulping process the tall oil components are saponified into a soapy material that, when acidulated, gives a mixture of free rosin and fatty acids and neutral components – crude tall oil. Crude tall oil is refined mainly by vacuum distillation processes to separate the various compounds almost completely into rosin and fatty acid fractions.

The *rosin* part of crude tall oil is a complex mixture of rosin acids, a three-ring fused system with the empirical formula $C_{20}H_{30}O_2$ (→ Resins, Natural, Chap. 5.2.3., → Resins, Natural, Chap. 5.4.). The tall oil *fatty acids*, primarily C_{18} types, are similar in composition to those derived from soybean oil. The *neutral constituents* of tall oil – predominantly esters, sterols, and hydrocarbons – are generally regarded as troublesome "impurities" that impair its utilization and distillation.

Abbreviations of basic tall oil names and common analyses are often used in publications and reports.

Crude tall oil (CTO) [*8002-26-4*]
Tall oil fatty acids (TOFA) [*61790-12-3*]
Tall oil rosin (TOR) [*8052-10-6*]
Distilled tall oil (DTO) [*8002-26-4*]
Tall oil pitch (TOP) [*8016-81-7*]
Heads, light ends (H) [*65997-03-7*]

2. Crude Tall Oil as Byproduct and Raw Material

The kraft pulping process was developed late in the 19th century. Some years later it was discovered in Sweden that a product similar to oil or wood tar could be obtained when the soapy material was acidulated with sulfuric acid. The recovery of byproducts from the kraft pulping process is shown in Figure 1 (see next page).

Tall Oil Precursor in Pine Wood. Exploitation of the original tall oil materials in pine wood in the form of products such as tar and pitch dates from centuries B.C. Gum and wood rosin are still produced, and compete with the rosin fraction, TOR, derived from CTO.

Products such as gum rosin (residue product, → Resins, Natural, Chap. 5.2.1.), and turpentine

10.1002/14356007.a26_057

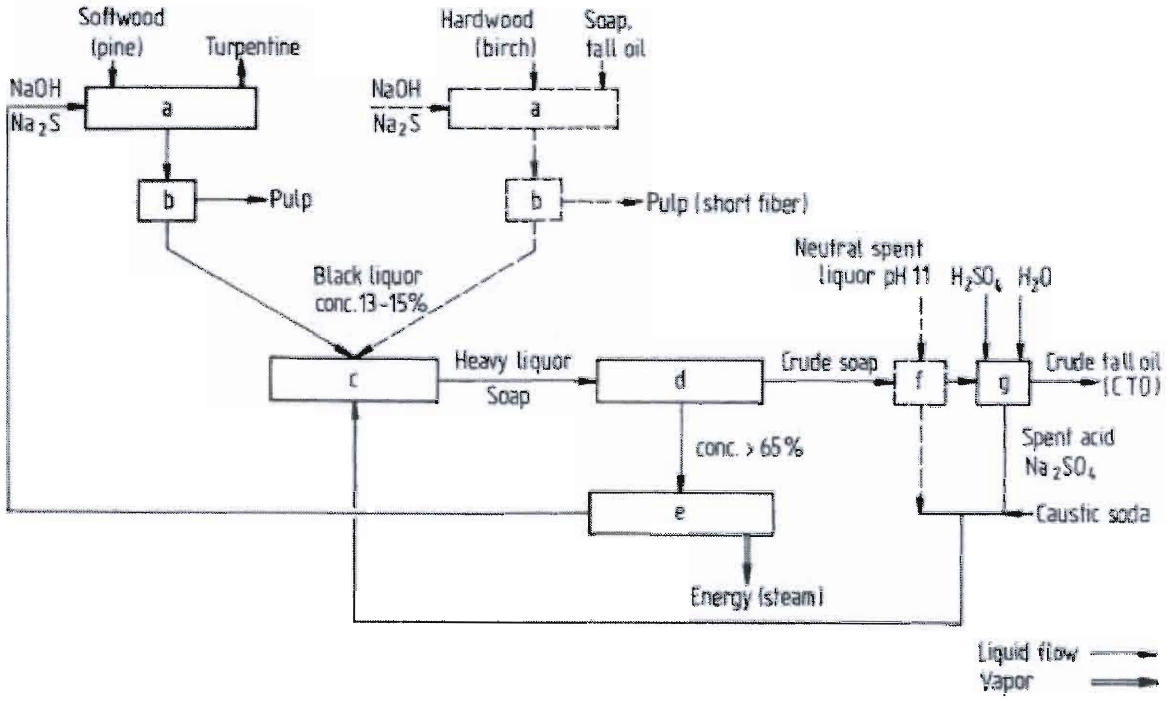

Figure 1. Recovery of byproducts from the kraft pulping process
a) Digester; b) Filter; c) Evaporator; d) Settling tank; e) Chemical recovery, energy production; f) Washing; g) Reactor

oil fractions (→ Turpentines) (distillates) obtained by distillation of exuded oleoresin from wounded living trees are still of high volume and importance. However, gum rosin production in the United States has declined drastically from ca. 300 000 t/a in 1930 to almost zero today owing to the lack of affordable labor. Despite this fact, worldwide gum rosin production in the early 1990s has been reported to be as high as 700 000 t/a. The People's Republic of China alone reports 400 000 t/a. Extraction of products such as wood rosin and turpentine fractions from stumps rich in rosin and liquid gum has declined because of the shortage of stumps (→ Resins, Natural, Chap. 5.2.2.).

Replacement of Original Products by Tall Oil. The production of CTO as a byproduct of the kraft pulping process and the subsequent refining of CTO have supplied important and renewable resources such as tall oil rosins and tall oil fatty acids as two basic chemical raw materials. The decreasing supply of wood and gum rosin in the United States is well compensated by the TOR production, which has increased proportionally to pulp production (see Fig. 2).

Tall Oil in Wood. The extractable portion of wood differs chemically, in part, from the compounds found in the CTO product. The chemical changes occurring during various processing steps are shown in Figure 3. Examples of composition of the extract from different wood species are listed in Table 1.

Table 1. Composition of the extract from different wood species

Compounds	Pine	Spruce	Birch
Esters, %	40	43	58
Free fatty acids, %	18	10	6
Free rosin acids, %	34	25	0
Total, %	92	78	64

2.1. Composition and Properties of Crude Tall Oil

The wide range of compositions and properties of crude tall oil on the market can be explained and understood from the chemistry of tall oil. Many tall oil components are sensitive to chemical reactions and changes in properties and composition. The use of wood species other than pine [e.g., spruce and hard wood (birch)] in the kraft pulping process lowers the yield of CTO and the selection of available fatty and rosin acids. It also changes the composition and properties of the CTO. The quality and yield of CTO from

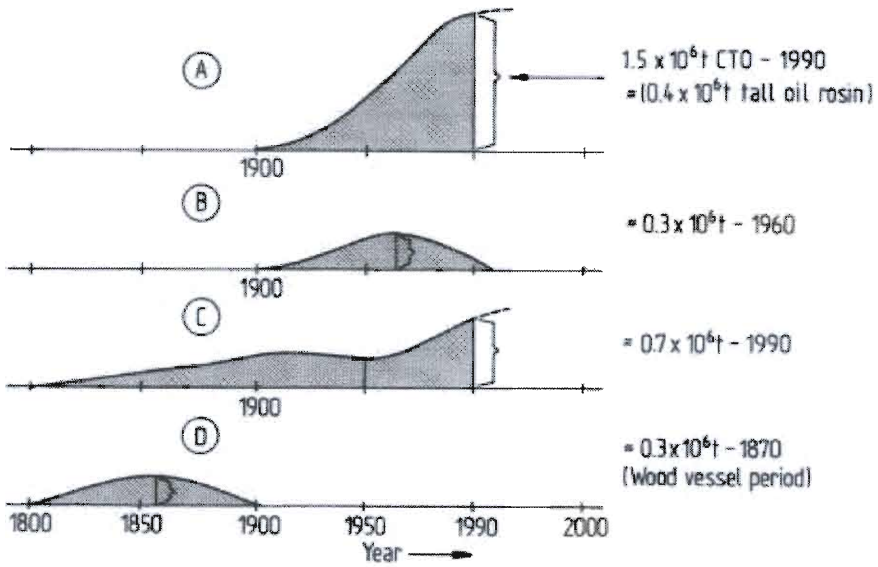

Figure 2. Historical development of global production of tall oil materials
A) CTO; B) Wood rosin; C) Gum rosin; D) Tar

the kraft pulping process consequently depend on many variables such as type and length of wood storage, season of the year, amount of wood residue used, hardwood usage, and type of pulping employed.

Table 2. Primary constituents of tall oil in different wood species

	Extractives, %	Fatty acids, kg/t wood	Rosin acids, kg/t wood	Unsap *, kg/t wood
Pine	≈ 3	15 – 20	5 – 10	2 – 5
Spruce	≈ 1	4 – 8	1 – 2	1 – 3
Birch	≈ 2	12 – 18		5 – 10

* Unsaponifiables.

Crude tall oil is a dark brown, tarlike product; its odor, influenced by sulfur components from pulp processing and soap skimming/acidulation, is unpleasant and penetrating. The three main constituent groups – fatty acids, rosin acids, and neutral materials (unsaps) – vary widely in composition, depending on the wood's origin (see Table 2). The saponification number (SN) of CTO is always higher than the acid number (AN) because of the unsplit esters in the crude oil. The difference increases for lower qualities, indicating less available rosin and fatty acids.

The crude is normally transported and stored at 50 – 80 °C to avoid crystallization and settling of rosin acids. The viscosity of the crude is variable; it is mainly a function of the rosin content. Viscosity must be measured on a clear, noncrystallized product. Impurities such as lignin, soap residue, water – oil emulsions, sodium salts, and sulfuric acid occur in the product. The amount of these undesirable materials depends on the efficiency of the soap washing and splitting process. Sour components such as sulfuric acid in the separated brine and degassed sour vapors from heated CTO in storage tanks impart the crude corrosive properties. The physical properties of tall oil (empirical values) are listed below:

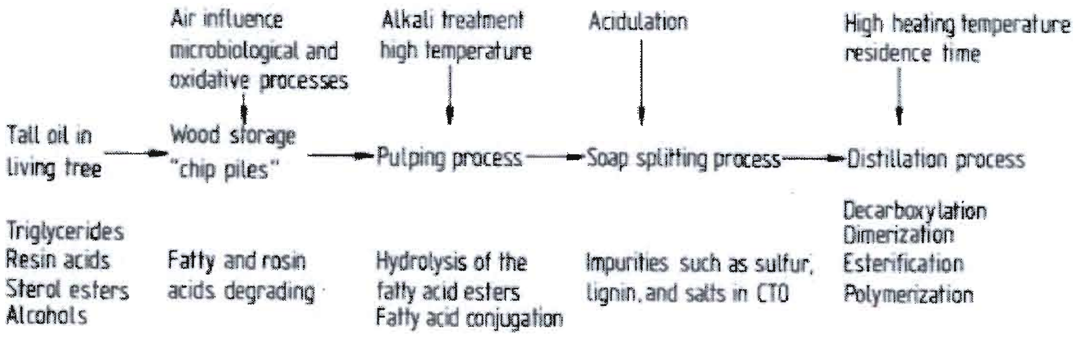

Figure 3. Chemical changes in tall oil during processing

Table 3. Typical data and composition of crude tall oil

Characteristic		Scandinavia, typical mix	United States, pine	Canada, mixed	France
Acid number		145	165	140	165
Saponification number		160	172	165	172
Fatty acids, %		45	45	42	40
Palmitic	(16:0)*	1.5	3	2	2
Stearic	(18:0)*	0.5	1	1	1
Oleic	(18:1)*	10	20	10	15
Linoleic	(18:2)*	17	13	15	11
Pinolenic	(18:3)*	5	1	3	1
Arachidic	(20:0)*	1	0.5	1	0.5
Other		10	6.5	10	9.5
Rosin acids, %		30	42	30	50
Pimaric		2	3	2	5
Palustric		4	7	5	7
Isopimaric		2	4	4	4
Abietic		12	15	10	18
Dehydroabietic		5	4	4	5
Neoabietic		4	6	3	6
Others		1	3	2	5
Neutrals, %		25	13	28	10
Moisture				$< 2\,\%$	
Ash				$< 0.2\,\%$	
Mineral acid (H_2SO_4)				$< 0.02\,\%$	
Sulfur				$< 0.3\,\%$	

Boil-up temperature (at 1.33 kPa)	180 – 270 °C
Heat of vaporization	290 – 330 kJ/kg
Specific heat	2.1 – 2.9 J/g
Heat of combustion	−(33 000 – 38 000) kJ/kg
Density (at 20 °C)	950 – 1020 kg/m^3
Liquid viscosity (at 70 °C)	25 – 40 mm^2/s

Typical data and composition of crude tall oil are presented in Table 3.

2.2. Recovery of Soap and Conversion to Crude Tall Oil

During the kraft pulping process, CTO precursors are hydrolyzed to soluble sodium soaps in the cooking liquor. The soap and spent cooking liquor (black liquor) are washed and filtered from the pulp and concentrated in multipleeffect evaporators from 13 – 15 % to > 65 % solids. Evaporation increases the solids content so much that the soap – contaminated with black liquor to a greater or lesser extent – precipitates and rises continuously to the surface of the upgraded liquors in skimming tanks connected to the evaporation process. When the soap is skimmed from the top of the black liquor tanks, contamination of the soap with some black liquor is unavoidable. The major part of this black liquor containing about 10 % lignin should be removed. Otherwise, precipitation of the lignin and gypsum (gypsum is formed because of the presence of calcium in the black liquor) will occur during subsequent acidulation. Good decantation or separation of the soap is thus important. A low black liquor content of the soap decreases acid consumption and the amount of toxic hydrogen sulfide and carbon dioxide released during acidulation. In addition, soap present in black liquor and in the heavy black liquor (i.e., concentrated black liquor) decreases the capacity of both the evaporator system and the recovery boiler.

The *splitting* or *acidulation process* is a chemical reaction between the sodium soaps and sulfuric acid. The tall oil soap is converted into free fatty and rosin acids by reaction with dilute sulfuric acid (ca. 30 %) at elevated temperature (ca. 98 °C). The reaction can be summarized as follows:

$$2\,RCOONa + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,RCOOH$$

where R denotes a rosin or fatty acid alkyl group.

Three phases are formed during the reaction: liberated tall oil, a lignin – fiber phase, and the spent acid phase (Na_2SO_4, free H_2SO_4). The phases can be separated because of their different densities. The splitting process is performed

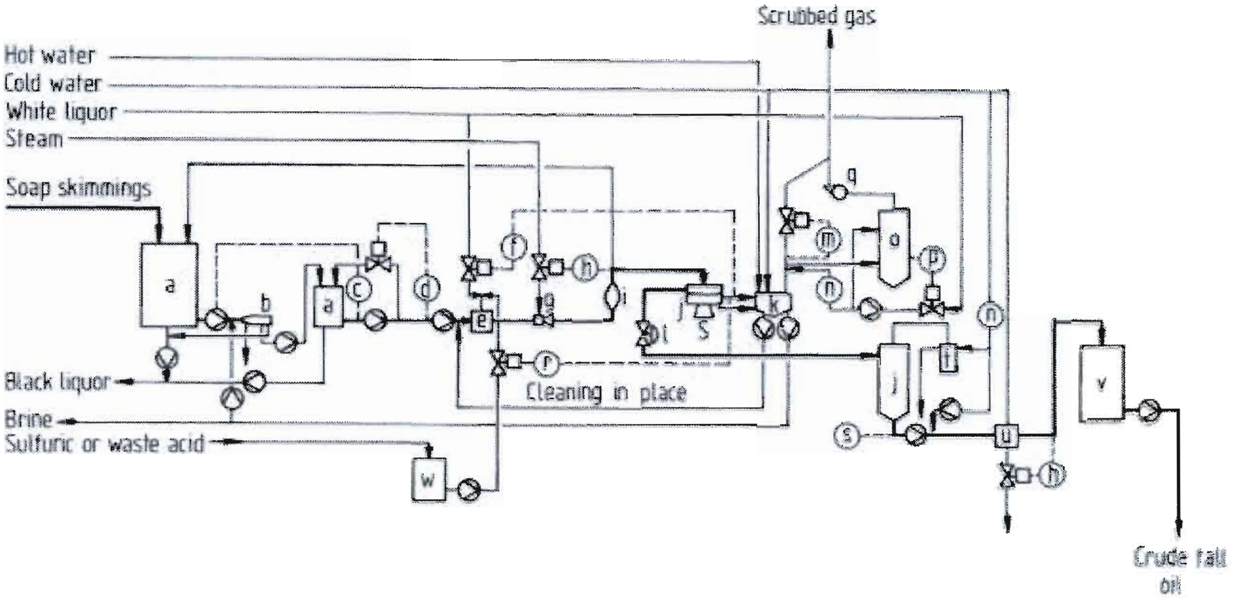

Figure 4. Hedemora – Celleco continuous tall oil system
a) Soap tank; b) Decanter – centrifuge; c) Level transmitter; d) Pressure transmitter control; e) Mixing-in piece; f) Density control; g) Direct steam heater; h) Temperature control; i) Reactor; j) Centrifugal separator; k) Brine tank; l) Constant pressure valve; m) Pressure switch; n) Flow meter; o) Gas scrubber; p) Liquid control; q) Fan; r) pH control; s) Temperature transmitter; t) Condenser; u) Tall oil cooler; v) Tall oil tank; w) Acid tank

either batchwise or continuously. In both cases the equipment must be made of acid-proof material, able to resist dilute sulfuric acid (spent acid or brine) at 90 – 100 °C. A pH of 2.5 – 3.5 is normal for complete reaction with a minimum of equipment corrosion. The Hedemora – Celleco continuous tall oil system is shown in Figure 4.

2.3. Upgrading of Soap Extraction (Crude Soap Refining Process)

On a limited scale, crude birch – pine soap is upgraded by extraction of neutrals before acidulation. The crude soap refining (CSR) process developed by HOLMBOM and AVELA in Finland yields not only a cleaner CTO but also commercial compounds such as sitosterols, terpenes, and aliphatic alcohols from the extracted neutrals. This upgrading process has been in operation since 1977 (Kaukas, Finland).

3. Upgrading of Crude Tall Oil by Distillation

History. In 1930 – 1950 a number of relatively small distillation plants (< 10 000 t/a) came onstream in Scandinavia and the United States, producing rosin-rich distillates and distilled tall oil. The “rosin oil” fractions were crystallized and centrifuged. The rosin crystals (rosin acid content ≈ 90 %) were melted and partly saponified.

The amorphous *rosin product* replaced gum and wood rosin in Scandinavia and was used in the Delthirna process for making paper size. The *distilled tall oil fraction* (rosin acid content 20 – 30 %) – in Scandinavia named “såpolja” (soap oil) – was used to make laundry soaps, as gel and solid products.

The introduction of *Linder trays* in fractionation towers was a promising alternative to already existing “dry” distillation (randomly packed) column processes. The first Linder plant came onstream in 1947 at Mo och Domsjö, Sweden as a dry distillation process designed for a rosin fraction introduced at the bottom of the column. The tall oil flow followed a convoluted path through a series of trays, encountering vapors generated in an electrically heated reboiler at the bottom of the column. Later, several Linder plants came onstream, further developed to produce TOFA with a low rosin content.

In 1949, Arizona Chemical and E. R. Badger introduced a *“wet” distillation process* in the United States, based on the experiences and techniques of the petroleum industry. This dis-

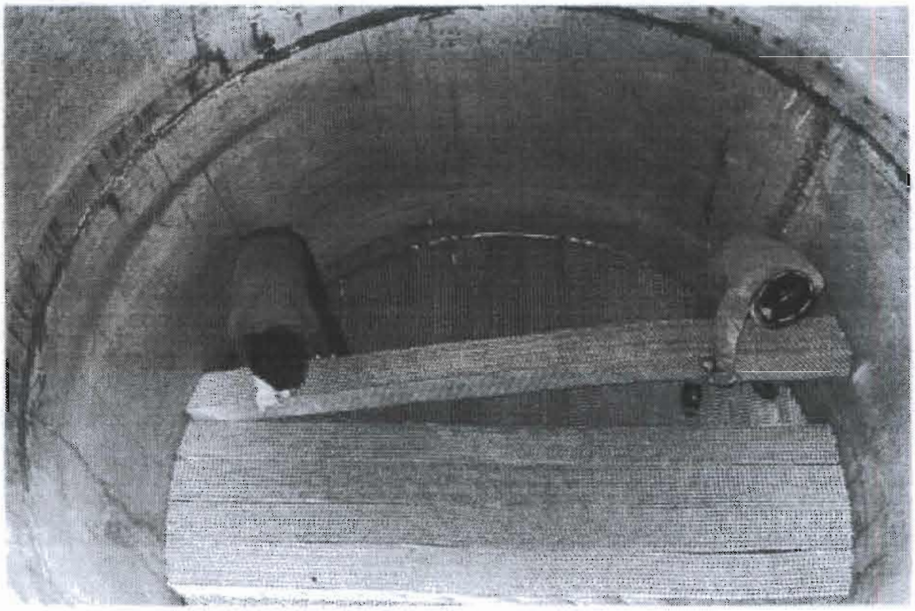

Figure 5. Sulzer's structured packing

tillation differed from the Scandinavian process. The use of bubble-cap towers for distillation made the addition of steam necessary for vaporization of the high-boiling tall oil components. To achieve sufficient separation of the fatty and rosin acids, a considerable number of trays is required. To overcome the high static pressure drop in the column, sparge steam must be used to avoid undesirable reactions of the products, caused by too high boil-up temperatures. Initially, the Arizona plant came onstream as a two-pass operation in a two-column system. The feed of the first pass is CTO, that of the second the crude fatty acid fraction from the first pass.

In 1970, Luwa, Switzerland built a plant for Krems Chemie in Austria using Luwa *thin film evaporators* for dehydration, depitching, and heat exchange for boil-up in the fractionation tower (packed columns). This approach minimized the time during which heat-sensitive compounds in tall oil were exposed to elevated temperature.

The introduction of *large-scale structured packing* (Mellapak, Sulzer Chemtech, Switzerland, see Fig. 5) at the Bergvik plant in 1979 improved the efficiency and capacity of the towers to achieve more complete fractionation of the vaporized high-boiling compounds in CTO. Worldwide, approximately 15 – 20 rosin columns and approximately 10 – 20 fatty acid columns equipped with structured packings are onstream today. A capacity comparison of two equal rosin columns, one of which is equipped with structured packing (Mellapak), is given in Table 4.

Table 4. Comparison of the capacity of two equal rosin columns

Characteristic	Pallring/minirings	Mellapak
Top pressure, kPa	0.2	0.2
Bottom pressure, kPa	1.6 – 2.0	0.8 – 1.2
Bottom temperature, °C	270 – 280	255 – 265
Capacity, t/a	40 000	80 000
Reflux ratio	4	2

3.1. Technical and Economic Conditions

Lengthy development work was required from the time CTO was discovered until a scientifically designed distillation process was achieved. Process performance may differ depending on local conditions, CTO quality, capacity demand, operation control equipment, and in-plant experiences, but the technology advances introduced have resulted in plants all over the world that are capable of producing fatty and rosin acid fractions of very high purity and quality. Special arrangements – mainly for the rosin fraction – were necessary because of variations in the quality of the CTO. However, these changes enabled the production of fractions with specific composition and properties. In practice, distillation of CTO has been achieved in two ways, both carried out in vacuum and at elevated temperature. The

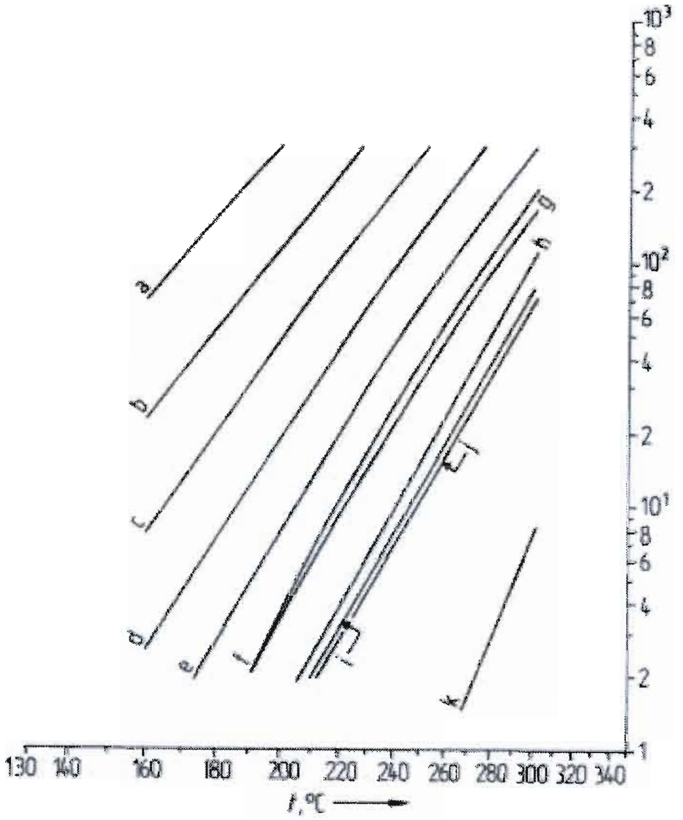

Figure 6. Vapor pressure curves of tall oil components (log $p - 1/t$ curves, t in °C is depicted on $1/t$ axis for convenience)
a) Caprylic acid ($C_8H_{16}O_2$); b) Capric acid ($C_{10}H_{20}O_2$); c) Lauric acid ($C_{12}H_{24}O_2$); d) Myristic acid ($C_{14}H_{28}O_2$); e) Palmitic acid ($C_{16}H_{32}O_2$); f) Oleic acid ($C_{18}H_{34}O_2$); g) Stearic acid ($C_{18}H_{36}O_2$); h) Arachidic acid ($C_{20}H_{40}O_2$); i) Abietic acid ($C_{20}H_{30}O_2$); j) Behenic acid ($C_{22}H_{44}O_2$); k) Heavy neutrals
(Courtesy of Sulzer Chemtech AG)

high-boiling components of tall oil can be vaporized either in the presence of superheated steam (wet process) or without adding any steam at all (dry process). In both cases, low pressure is necessary to vaporize the high-boiling compounds. At actual operating temperature the compounds are sensitive to undesirable chemical reactions, depending on heating conditions. In addition, the compounds degrade rapidly in the presence of oxygen. Therefore, the entire apparatus involved in distillation must have the functional security sufficient to meet the demand of steady running.

The "dry" process is more favorable today than the "wet process"; it involves lower energy costs and less air and water pollution. The Swiss technology – rapid heating for boil-up and improved mass transfer at lower pressure drop and lower reflux ratios – for distilling CTO has been successful and used completely or partly in new and upgraded plants all over the world.

The trend in the tall oil field has been toward increased capacity, in order to gain scaleup effects, meet pollution restrictions, and produce tall oil fractions that are suitable for further processing into specific products. To obtain this, computerized control facilities are generally necessary and of great importance. Most of all, a stable operating pressure (vacuum) must be maintained to obtain fractions that meet certain values and limits. Even a small pressure change results in different process temperatures, corresponding to the new pressure. Improved techniques and resistant materials, more suited for treatment of high-boiling and heat-sensitive tall oil compounds, have led to the development of efficient distillation processes. The vapor pressure curves of tall oil components are depicted in Figure 6. The residence time of the product and the temperature differences between the product and the heating medium in different reboilers (see Table 5, next page) influence product quality and yield. Therefore, heating conditions are very important.

As heating medium Dowtherm (→ Hydrocarbons) is often used in liquid form. The desired or programmed product temperature and

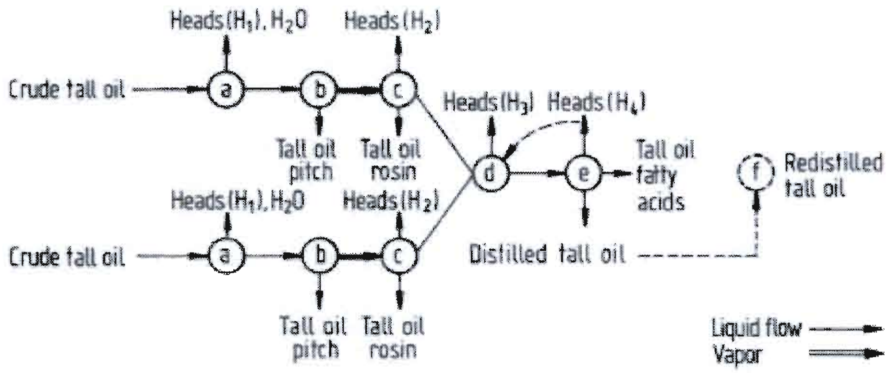

Figure 7. Simplified flow sheet for large-capacity plants (>100 000 t/a)
a) Dehydration; b) Depitcher; c) Rosin column; d) Light ends column; e) Fatty acid column; f) Distilled tall oil columns

composition can be established with great precision at each heating station by regulating the amount of Dowtherm liquid flow in the loops connected to the head coil.

Dowtherm in vapor form as heating medium is still used mainly in U.S. plants, in a way similar to conventional steam-heated systems.

The principal flow sheet for the tall oil distillation process is, in practice, quite old. A simplified flow sheet of a large-capacity plant (> 100 000 t/a) is given in Figure 7. The Bergvik Kemi tall oil plant is shown in Figure 8.

Table 5. Residence time and Δt (temperature difference between heating medium and product) for different types of reboiler

Type of reboiler	Residence time	Δt, °C
Forced circulation	≈ 60 min	≈ 5
Thin-film evaporator with fixed wipers	≈ 5 s	≈ 40
Falling-film evaporator with circulating pump	1 – 2 min	≈ 15

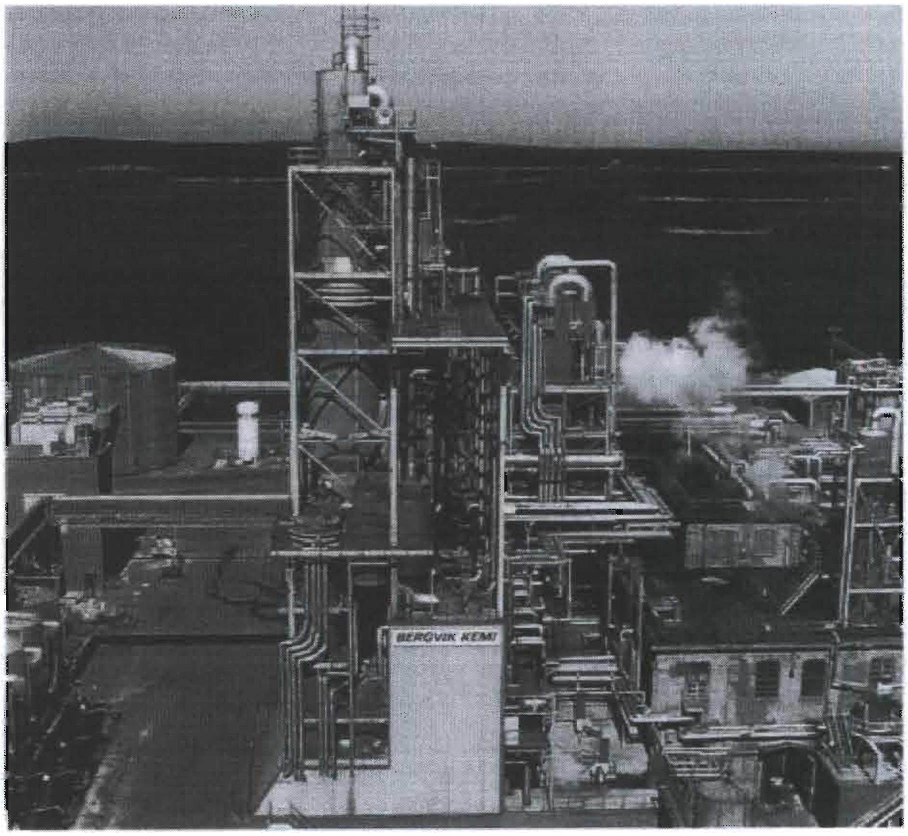

Figure 8. Bergvik Kemi tall oil plant

3.2. Process Description

3.2.1. Dehydration

CTO is fed directly from the storage tank into the thin-film evaporator (Fig. 7, a) for rapid preheating up to 200 °C under vacuum (3 – 6 kPa). Inert combustible gases, water ($\approx$1 %), low-boiling compounds such as organic heads (H_1) and turpentine ($\approx$1 %) are distilled during the first passage through the evaporator. This operation makes possible a stable low pressure ($\approx$ 0.3 kPa) in the dry distillation and fractionation of the relatively high-boiling tall oil components that follow.

3.2.2. Depitching

The applicability of dry distillation not only is influenced by the CTO composition but is also highly dependent on conditions [e.g., operating pressure and temperature and residence time of the products in the depitcher (Fig. 7, b)].

The vaporization and squeezing of vaporizable products, such as separation of the fatty and rosin acids from native pitch compounds in CTO and from pitch formed by heating, require a high temperature (270 – 275 °C), even at low pressure (800 – 1300 Pa), measured at the vapor entrance into the rosin column or the first fractionation tower. The optimal depitching conditions for obtaining maximum yields and purity of rosin and fatty acid fractions are, however, of delicate nature. At elevated temperature undesirable reactions can occur such as esterification of fatty acids (by alcohols contained in the CTO), polymerization, decarboxylation of rosin acids, and isomerization of abietic-type acids. Too high a depitching temperature also leads to decomposition and vaporization of high-boiling compounds (neutrals, fatty acids) that affect the quality of rosin and fatty acid fractions negatively.

3.2.3. Fractionation of Vaporized Tall Oil Compounds

To reduce the pressure drop and achieve the lowest possible pressure in the depitching step the top section of the rosin column has a wider diameter than the lower section. Overhead vapor from the depitcher, consisting mainly of rosin and fatty acids but also of nonacidic compounds, is fed to the rosin column (Fig. 7, c) to recover rosin as a bottom fraction (TOR). The rosin acids in TOR are similar in composition to those found in gum and wood rosin. As distillate (side stream from the upper part of the column) the crude fatty acid intermediate fraction, containing about 8 % rosin acids, is taken off and fed to the light ends column (d) to remove light heads (a mixture of neutral compounds and short-chain fatty acids). The bottom fraction, containing mainly C_{18} fatty acids, a smaller portion of rosin acids, and a "minimum" of neutrals, is then fed to the fatty acids column (e) for production of high-quality tall oil fatty acids as a side stream from the top section of the column. From the top of all involved fractionation towers, smaller cuts of head fractions containing mixed neutrals and "low-boiling" ($C_8 - C_{16}$) fatty acids are distilled off ($H_1 - H_4$).

Distilled tall oil containing most of the rosin acids in the intermediate or crude fatty acid fraction, is usually distilled off as a side stream "middle-boiler" fraction as well as by other means, depending on local technical conditions and feed composition.

The fatty acids in CTO are mainly C_{18} unsaturated acids ($\approx$ 85 %) in which a significant proportion of the linoleic acid has been isomerized to the conjugated acid during the alkaline pulping process. The rest of the fatty acids are – if compared to the C_{18} compounds – of "low-boiling" and "high-boiling" character. More than 20 different acids from C_8 to C_{24} have been identified, among which palmitic, stearic, eicosanoic, arachidic, and behenic acids are of most interest. The higher-boiling fatty acids are concentrated mainly in the DTO fraction by fractional distillation, but are also contaminants in the rosin acid fraction. Depending on the conditions during pulping and distillation, some abietic types are isomerized to dehydroabietic acid.

Both the tall oil fatty acids and the rosin acids contain two functional groups: double bonds and the carboxyl group, which allow a number of chemical reactions. Some of these occur during processing, depending on CTO composition and external physical and chemical influences. These reactions result in increased pitch yield (by esterification, polymerization, oxidation) or

Table 6. Principal composition and yields of tall oil fractions and some empirical volatility data

Fraction	Yield, %	Acid number	Composition, %		
			Rosin acids	Fatty acids	Neutrals
Head	5–12	70–120	<0.5	30–50	40–60
TOFA	35–45	192–197	<2	95–98	1–2
DTO	5–15	180–190	20–30	65–70	4–7
TOR	20–35	165–182	85–96	1–5	1–7
TOP	20–40	20–50	5–13	5–10	40–60

affect the molecule structure of certain sensitive materials (e.g., isomerization of linoleic acid in the fatty acid group). Levopimaric acid is converted to more stable forms, and other isomers of abietic acid are formed.

The principal composition and yields of tall oil fractions are listed in Table 6.

4. Energy Recovery

Like many other distillation processes characterized by several steps and elevated temperature (150–300 °C), the energy demand of tall oil distillation is large and costly. Thus, operating the distillation column at low reflux ratios and reusing the energy from the condensation system as heat (i.e., for the distillation process and for supplementary equipment, tanks, etc., belonging to a complete tall oil plant) is very important in terms of economics.

Besides the usual arrangements for heat exchange of hot and cold streams in the process, most of the thermal energy from the condensation system can be transformed into low-pressure steam (see Fig. 9). The quantity of low-pressure steam in principle meets the demands of the tall oil process. It is used mainly in vacuum jets and CTO tanks but also for other heating purposes.

5. Security and Construction Material

Acceptable construction material and process equipment that resist the corrosivity of tall oil compounds – particularly fatty acids – ensure reliable operation. Based on many years of "dry" distillation, the Co–Ni–Mo alloy, containing 2.5 % molybdenum (AISI Type 316) was regarded as an acceptable material, combating cor-

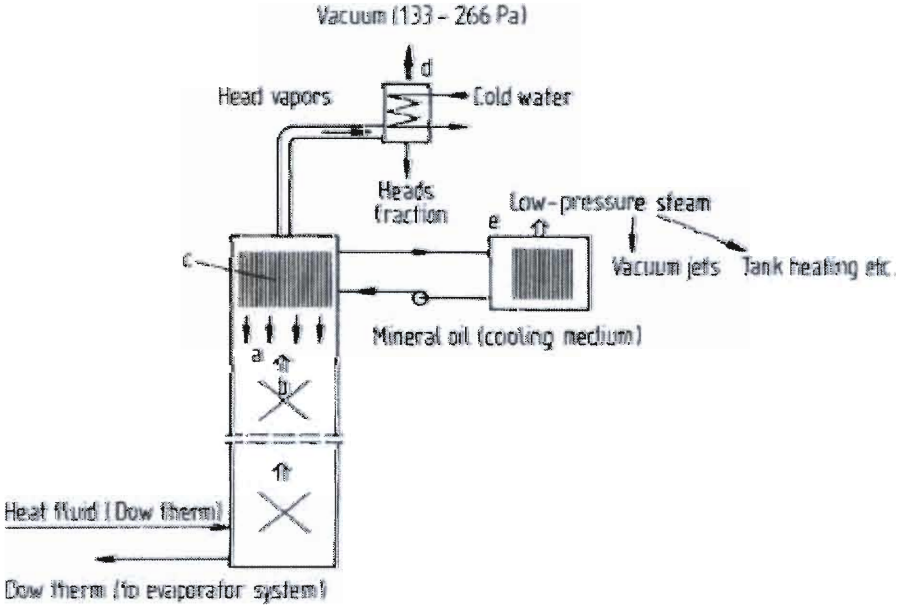

Figure 9. Heat recovery system
a) Fractionation tower; b) Flexipack packings (corrugated Al sheet); c) Deflegmator (partial condenser); d) End counter; e) Steam generator station

rosion generally in the tall oil distillation process. However, as time went on, the corrosion of replacement parts occurred, sometimes followed by unscheduled shutdowns and quite often fires. This resulted in the use of an alloy containing more than 3.5 % molybdenum (AISI Type 317).

Vapor-phase streams are more corrosive than liquid-phase streams, and corrosion increases with increasing temperature. The corrosion rate of alloys with 5 – 6 % molybdenum is negligible; thus, the use of high-molybdenum alloy in construction of the equipment is essential. Aluminum has been used for tanks, pipelines, packings, etc., and is still of interest when special strength is not required.

6. Analysis

Most of the analytical methods for tall oil are established standards and, as such, collected in ASTM and especially in SCAN (Scandinavian Pulp Paper Testing Committee) publications. About 20 standard methods are available.

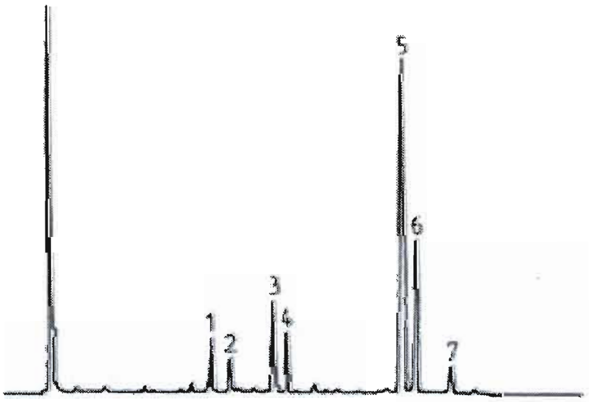

Figure 10. Gas chromatogram of tall oil rosin
1. Pimaric acid; 2. Sandaracopimaric acid; 3. Palustric acid; 4. Isopimaric acid; 5. Abietic acid; 6. Dehydroabietic acid; 7. Neoabietic acid

In addition to the standard methods of analyses, gas – liquid chromatography, mass spectroscopy, and gel permeation chromatography are used widely for better understanding of tall oil chemistry. A gas chromatogram of tall oil rosin is shown in Figure 10. These methods are essentially necessary complements to the older standard analyses for further development of the processes and of special or unique products as well. Typical data and composition of tall oil fatty acids and of tall oil rosins are listed in Tables 7 and 8.

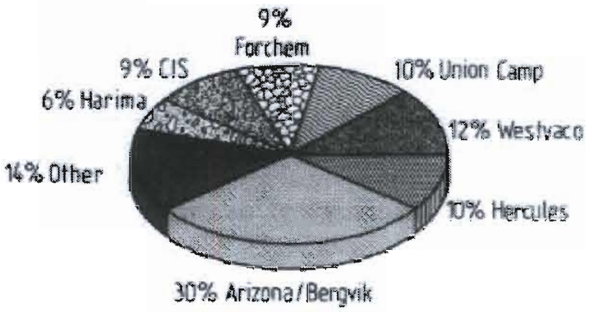

Figure 11. World tall oil fractionation capacity by company

Table 7. Typical data and composition of some tall oil fatty acids

		Scandinavia	United States
Acid number		195	197
Rosin acids, %		2	1
Unsap ∗, %		2	1.5
Iodine value		150	130
Color, Gardner		4	3
Fatty acids, %			
Saturated		2	2
Oleic	(18:1)	30	48
Linoleic	(18:2)	44	37
Linolenic	(18:3)	10	3
Conjugated	(18:2)	6	6
Other		4	2.5

∗ Unsaponifiables.

Table 8. Typical data and composition of some rosin types

	Gum rosin	Wood rosin	Tall oil rosin		
			United States	Scandinavia	
				I	II
Acid number	167	157	174	173	180
Rosin acids, %	90	85	92	90	95
Fatty acids, %			2	4	2
Softening point, °C	78	73	75	66	75
Color, USDA∗			WW	X	XA
Composition of rosin acids fraction, %					
Pimaric	7	7	2	3	3
Palustric	20	8	7	8	7
Isopimaric	15	15	8	6	6
Abietic	30	50	40	40	40
Dehydroabietic	5	8	20	22	23
Neoabietic	15	5	3	4	4

∗ For a definition of USDA color shades, see → Resins, Natural, Chap. 5.4.

Table 9. Applications of tall oil fractions

Composition, uses	Pitch	Rosin	Distilled tall oil	Fatty acids	Heads
Principal composition	esters, sitosterol, estolides, rosin dimer, free fatty and rosin acids	rosin acids (isomeric diterpene acids, complex mixture), free fatty acids, neutrals, unsaps 3 – 10 %, esters	fatty and rosin acids, neutrals, unsaps, esters < 10 %	fatty acids (oleic, linoleic types > 90 %), rosin acids (neutrals < 10 %)	fatty acids (saturated)
As intermediates in miscellaneous processes	mixtures for chemical modification	fortification, Diels – Alder reaction, dimerization (catalytic process), isomerization, esterification, disproportionation	alkyd formation, esterification, saponification, epoxidation	dimerization, isomerization, esterification, alkyd formation, saponification, separation, ethoxylation, decarboxylation, C_{21} diacids	mixtures, crystallization (palmitic acid)
Final uses	fuel, binders, coatings, rubber modifier, asphalt, sizing, printing inks, hardboard impregnation	paper size, protective coating, adhesive, ink, rubber, hot melt	soap, coating, flotation, board impregnation	protective coating, soap, ink	fuel, flotation, asphalt emulsifier

7. Storage and Transportation

The crude tall oil, melted rosin, and pitch are stored at elevated temperature to reduce viscosity. Air exposure of both fatty and rosin acid fractions results in darkening of the products. Protection with inert gases – N_2, CO_2, and steam – at elevated temperature is recommended. The fatty and rosin acid fractions are preferably stored and shipped in tanks made of stainless steel or aluminum. When rosin in the melted state is shipped in insulated tank cars, the temperature is kept at > 160 °C. Rosin derivatives should be produced in direct connection with the distillation process. By storing rosin in solid form (galvanized drums), additional costs (packaging, handling, remelting, etc.) may arise. In addition, TOR in drums can crystallize easily to become nonbrittle and often difficult to remove. Today, the modified resin products are generally flaked or compressed into tablets and delivered in paper bags.

8. Uses

Uses of CTO. Most of the world production of CTO ($\approx 1.5\times10^6$ t/a) is utilized as raw material in continuous distillation processes, producing high-quality tall oil fatty acid fractions and tall oil rosins as primary products. If the CTO is "low grade" (e.g., the content of valuable components is too low), the product (or the corresponding soap) is used as liquid (or solid) fuel. Since CTO, irrespective of quality, can always be used as a fuel oil, its minimum price is more or less related to actual "fuel oil" prices on the market, including taxes and other associated costs.

Tall Oil Fractions. The TOFA and TOR fractions are used widely for further processing into a variety of chemical products, replacing other raw materials such as gum and wood rosin, hydrocarbon resins, and vegetable oils. Improved distillation techniques have led to upgraded fractions of TOFA and TOR that are attractive raw materials for special chemicals. The chemical structure of some fatty and rosin acids makes the primary tall oil fractions suitable as raw material for making intermediate chemicals. Examples are the production of dimeric fatty and rosin acids, polymerized rosin, and maleic and fumaric anhydride (acids) – rosin adducts including their salts and esters (→ Resins, Natural, Chap. 5.5.). The dimeric acids are utilized as raw materials to make products used in adhesives, coatings, inks and epoxy resins. Most of the intermediate chemicals are processed in

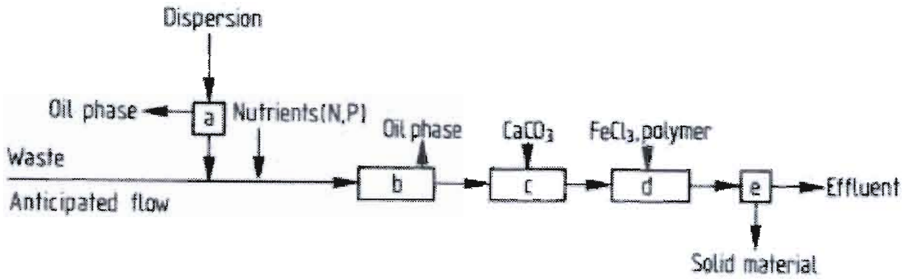

Figure 12. Principal waste treatment process
a) Phase separation equipment (Knitmesh filter); b) Oily water skimming basin; c) Aerotin basin (biological treatment); d) Chemical treatment basin; e) Filter, sludge decanter centrifuge
BOD reduction > 96 %; COD reduction > 88 %

the presence of certain catalysts. An overview of the applications of tall oil fractions is given in Table 9.

9. Economic Aspects

The total world production of CTO was in the range of 1.5×10^6 t in the early 1990s. Most of the available quantities are produced and refined in the United States and Europe. The world tall oil fractionation capacity by region is as follows:

United States	56 %
Scandinavia	21 %
Other Western Europe	7 %
Other	16 %

A breakdown of world tall oil fractionation capacity by company is given in Figure 11.

10. Toxicology and Environmental Protection

Toxicology. The tall oil compounds in living trees, stumps, CTO, fractions, etc., are nonhazardous natural substances. Modified tall oil products and solutions may, however, become hazardous because of the chemicals and solvents used. Many tall oil derivatives such as glycerol and pentaerythritol esters, alkyd resins, dimerized fatty acids, and rosin acids are generally regarded as nonhazardous products.

The toxicity of tall oil components in effluent water to fish is not a function of oxygen demand. Fish may tolerate some higher (allowed) concentration limits of rosin and fatty acids or their sodium soaps in the waste stream. These concentrations may be indicated along with the other conventional parameters (COD, BOD, etc.) of the wastewater.

Environmental Protection. During vacuum distillation, some product losses arise, resulting in polluted water and inert gases. The water streams from the various processes are of different compositions but after passing through special oil separation equipment, they are collected for the removal of organic waste constituents by biological, physical, or chemical methods before they are discharged (see Fig. 12). The noncondensed (odor) component of the gases may be disposed of as fuel gas if necessary.

The dry distillation method has the advantage of requiring fewer measures to combat pollution compared to the wet process. In distillation, most of the polluted water comes from the dehydration steps, where the "low-boiling" components (1 %) together with the water in CTO (1 %) are distilled off from the feed before depitching. Additional sources of polluted water are related to the steam jet vacuum systems, plant cleanup wastes, CTO storage tanks, pumps, etc.

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Tallow → Fats and Fatty Oils
Tanning Agents → Leather

Attachment 8, Section 9

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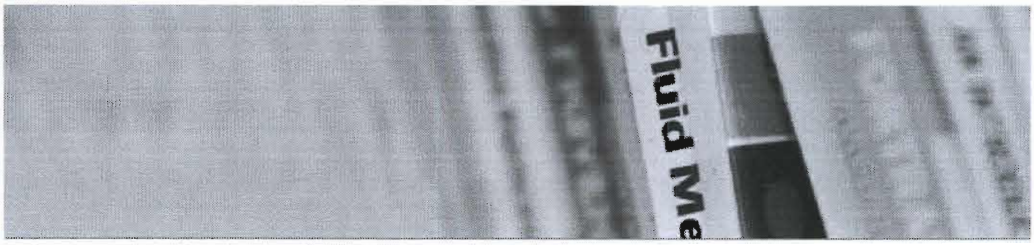

Titre du document / Document title
Gas chromatographic analysis of tall oil fractionation products after methylation with N,N-dimethylformamide dimethylacetal

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Résumé / Abstract
Tall oil fractionation products such as tall oil fatty acids, distilled tall oil, and tall oil rosin are routinely analyzed by gas chromatography (GC) after derivatization with diazomethane or esterification with methanol using boron trifluoride as a catalyst. An alternative derivatizing reagent, N,N-dimethylformamide dimethylacetal, has been investigated for the preparation of methyl esters of fatty acids and resin acids in tall oil fractionation products prior to GC analysis. This reagent provides a safe, rapid, and reproducible means of derivatization that eliminates the need to isolate the methyl esters from the derivatization reaction mixture.

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Attachment Study 1 and 2, Section 9

Attachment 9 and 10 Section 9 (page 2 and 3

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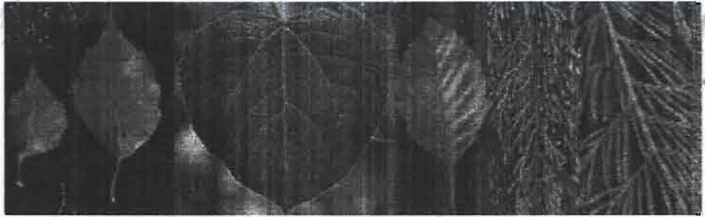

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Chemistry

Forest-based chemicals

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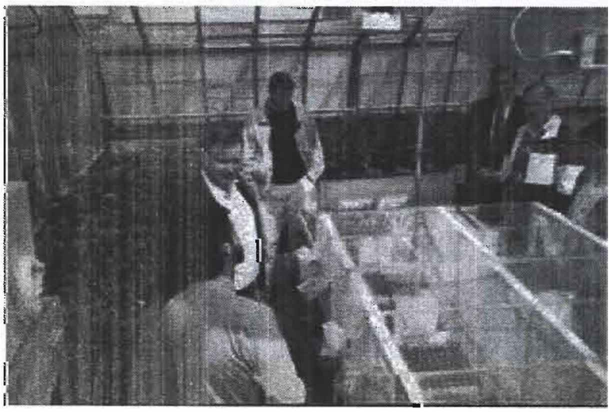

Tall oil, tall future

BC News, February 1991

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Publications

Acidulation of tall oil soap with phosphoric acid

Alfred Wong, J.M. Zhuang and Stanley Wu, Arbokem Inc., Vancouver, Canada

ABSTRACT. The use of H3PO4, instead of H2SO4, affords a novel approach to eliminate the input of sulphur into the pulp mill's chemical recovery system. Laboratory soap acidulation experiments have shown the H3PO4 soap acidulation approach to be practicable. The H3PO4 approach would provide the avoidance of adding about 27 kg sulphur (as S) per tonne of soap into the chemical recovery system of the kraft pulp mill. Under prevailing pricing of H3PO4 and NaOH, the phosphoric acid approach would have a higher chemical cost than the sulphuric acid approach, by a margin of about US$8 per tonne of soap processed. Small changes in the commodity pricing of H3PO4 and/or NaOH would render the H3PO4 soap acidulation method to be economically competitive. (AK21630W)

Cellulose Chemistry and Technology, 36: 381-388 (2002)

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attachment 9
section 9

Degradation of crude tall oil held under heated conditions.

Part 1 - Basic reactions and binary mixtures of model compounds.

Al Wong, Arbokem Inc., Vancouver, Canada

ABSTRACT. The degradation of model components of crude tall oil (CTO) held under heated storage conditions was studied. Rate constants for the reactions of stearyl alcohol and mixed tall oil sterols separately and in combination with oleic acid were determined. These reactions were found to be "first-order", in the range of concentrations which are representative of commercial CTO. The rate of esterification between oleic acid and stearyl alcohol was found to be about three times faster than that of the reaction between oleic acid and tall oil sterols. (AK24523W)

Forest Chemicals Review, 113 (2): 12-16 (2003)

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Degradation of crude tall oil held under heated conditions.

Part 2 - Ternary mixtures of model compounds and prediction of acid number decreases.

Al Wong, Arbokem Inc., Vancouver, Canada

Attachment 10, section 9
Study 2)

ABSTRACT. Acid number decreases of ternary mixtures of CTO model compounds, viz., fatty alcohol, sterol and fatty acid, were studied. A practicable means to estimate the rate and magnitude of acid number losses of CTO during heated storage has been devised, in which esterification and decarboxylation reactions were included. (AK23445W)

Forest Chemicals Review, 113 (3): 11-14 (2003)

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Terpene content of crude sulphate turpentine from selected kraft pulp mills of British Columbia and Alberta

Al Wong and Yi Feng, Arbokem Inc., Vancouver, Canada

ABSTRACT. Chemical analysis of selected samples of crude sulphate turpentine (CST) from several kraft pulp mills in inland British Columbia and Alberta showed the

pinene content to be less than 50% of those of CST of southern United States pulp mills. Both delta3-carene and para-menthadienes were found to be substantially higher than those present in CST of southern United States pulp mills. (AK21602W)

Forest Chemicals Review, 112 (1): 10-14 (2002)

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Sterols in soap and tall oil from North American kraft pulp mills

Al Wong, Arbokem Inc., Vancouver, Canada

ABSTRACT. Representative samples of soap and CTO from 17 kraft pulp mills using coniferous pulpwood grown in the major forest regions of North America were evaluated over a period of 5 years. There were notable differences in the quality and quantity of sterols in the CTO and soap tested. CTO from the Northern, Rocky Mountain and Pacific Coast forest regions was found to be the best for the practical isolation of sterols containing a high fraction of C29 sterols and stanols, which are favourable for use in anti-hypercholesterolemic products for human consumption. The Southeastern CTO contained the lowest amount of sterols, among the CTO surveyed in North America. (AK21183W)

Forest Chemicals Review, 111 (5): 12-17 (2001)

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Management of sulphur balance and tall oil production in unbleached kraft pulp mills

Al Wong, Arbokem Inc., Vancouver, Canada

ABSTRACT. Soap acidulation using sulphuric acid is a major source of involuntary input of sulphur into the cooking liquor system of a kraft pulp mill. The sulphur balance problem, under increasingly stringent rules for the discharge of pollutants, could be manageable if the mill produces a relatively lower amount of soap for acidulation with sulphuric acid. If new targets are mandated for COD in the effluent and hazardous air pollutants under the EPA Cluster Rules in the near future, pulp mills will have difficulties in the continuance of using any sulphuric acid for soap acidulation, without causing a sulphur imbalance in the mill liquor system. (AK19067W)

Forest Chemicals Review, 110 (4): 9-11 (2000)

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A novel method for the preparation of cellulose acetate

J.M. Zhuang and A. Wong, Arbokem Inc., Vancouver, Canada

ABSTRACT. An improved method has been developed for the preparation of high-quality cellulose acetate. The novel technique involves the pressurized pretreatment of cellulose fibres with glacial acetic acid and acetic anhydride. The resulting fibres were found to be more uniformly activated and more reactive in subsequent acetylation. With the anhyrdous pretreatment stage, direct addition of acetylation reagents can be carried out at higher initial temperatures. The hydrolysis of cellulose triacetate to cellulose diacetate was also found to be improved significantly when the reaction was controlled under elevated temperature and pressure conditions.

Proc. 8th International Symposium on Wood and Pulping Chemistry, Helsinki, Finland, June, 1995. pp. 685-688.

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Uloth, V.C., Ouchi, M.D., Wearing, J.T. and Wong, A., "**The Effect of Soap Acidulation Conditions on Tall Oil Production**", Proc. Tappi Pulping Conference, San Diego, USA, November, 1994.

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Ouchi, M.D., Uloth, V.C. and Wong, A., "**A Spectrophotometric Method for the Determination of Black Liquor and Lignin Content of Tall Oil Soap**", Naval Stores Review, 104, 1: 4 (Jan/Feb, 1994).

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Scientific research and commercial realization of forest-based chemical products

Alfred Wong, Arbokem Canada, Vancouver, Canada

ABSTRACT. During the past 100 years, there have been substantial activities made in the research and development of chemical products from renewable forest resources. Yet, commercial successes have been few. One underlying problem is the large gap between scientific knowledge and commercial realization. In many cases, the successes such as extraction of taxol from Pacific yew tree, can be easily identified to be in the category of chemical products of unique silvichemical structures. The failures can be traced to poor economic premises of commodity chemical products. Some recent successful and unsuccessful examples of "research to commercial manufacture" of silvichemical products will be presented to illustrate the problems of scientific research and commercial implementation. (AK10085W)

Proc. 7th International Symposium on Wood and Pulping Chemistry, Beijing, China, *May 25-28, 1993.*

Diterpene resin acids: Major active principles in tall oil against variegated cutworm, Peridroma saucia (Lepidoptera: Noctuidae)

Y. Xie and M.B. Isman, University of British Columbia, Vancouver, Canada
Y. Feng and A. Wong, Arbokem Inc., Vancouver, Canada

ABSTRACT. Tall oil, a by-product of the kraft process for pulping softwood, has been shown to have insecticidal properties. In the present study, the active principles in tall oil against the variegated cutworm, Peridroma saucia Hubner, were investigated. GC-MS analysis showed that abietic, dehydroabietic and isopimaric acids were major resin acid components of crude tall oil and depitched tall oil. When crude tall oil samples of differing resin acid composition were incorporated into artificial diet at a concentration of 2.0% fresh weight, they suppressed larval growth by 45-60% compared to controls. This suppression was significantly (P,0.05) correlated with the equivalent contents of abietic, dehydroabietic, isoprimaric, and total resin acids. These results were also evident from a diet choice test, showing that the second-instar larvae obviously selected diets with low levels of resin acids when different diets were randomly arranged in a Petri dish. Bioassays with pure resin acids (abietic, dehydroabietic, and isopimaric acids) demonstrated that all individual chemicals have similar bioactivity against this insect. Comparison of the bioactivities of depitched tall oil and an equivalent mixture of pure resin acids in the chronic Peridroma chronic growth bioassay indicated that pure resin resin acids and depitched tall oil share a common mode of action to this insect. This study

confirms that resin acids are the major active principles in tall oil against the variegated cutworm, but other chemicals likely also contributed to the bioactivity of tall oil.

Journal of Chemical Ecology, 19:1075-1084 (1993).

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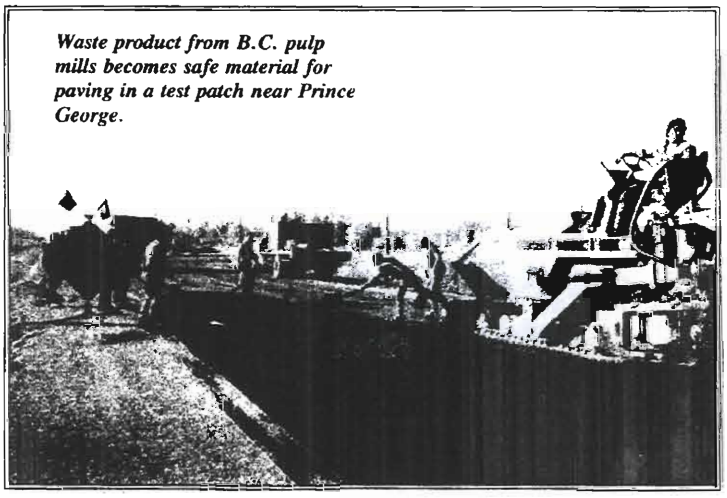

Waste product from B.C. pulp mills becomes safe material for paving in a test patch near Prince George.

Tall oil, tall future

A B.C. CHEMICAL COMPANY HAS become the first in Canada to develop a new line of clean and value-added products from tall oil, a co-product from the manufacture of wood pulp in the Interior.

B.C. Chemicals of Prince George says projects already confirmed and those still in development would create 46 new jobs and add $36 million to the provincial economy.

"It's a perfect example of obtaining more value-added products from a renewable resource and it does not require the harvesting of more trees," says B.C. Chemicals president Hugh Norman.

"In fact, it's a way of finding innovative use from the two per cent of a log that doesn't go from lumber to pulp."

Tall oil soap is recovered after interior spruce and pine wood chips are converted into pulp. Too difficult to burn safely in mills' recovery furnaces, tall oil soap is processed into crude tall oil. In the past it was exported to Japan and southern U.S.A.

Now the company aims to have virtually all the processing done in B.C., along with work that may lead eventually to the establishment of pharmaceutical and insect anti-feedant industries.

"Pulp now sells for about $750 a tonne but some of the things that can be made from tall oil could bring $10,000 a tonne," says Norman.

"A secure supply of sterol starting material from tall oil would provide a strong incentive to persuade drug-manufacturing companies to come to B.C.," he adds.

"Insect anti-feedant is a new class of naturally-occuring chemicals which alter the feeding behavior of insects. These insect anti-feedants don't harm the environment and they can be targeted to certain harmful insects, such as spruce budworm and Rocky Mountain pine beetles."

Last year B.C. Chemicals began producing upgraded tall oil and tall oil pitch at its new $8 million plant in Prince George. The new plant has been producing an extender for asphalt paving, and a new type of emulsion for the stabilization of unpaved roads.

B.C. Chemicals is working closely with Arbokem Inc. of Vancouver on additional tall oil technology projects. Arbokem has the world-wide rights to Canadian technology for making motor fuel additives from tall oil. They plan to have a technology prototype in operation in Prince George by the end of 1991. ☐

Attachment 11, section 9

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 85

THE REACTION OF TALL OIL FATTY ACIDS DURING SIMULATED OXYGEN-ALKALI DELIGNIFICATION. 1. EFFECTS OF REACTION VARIABLES

GERALD R. MITTET AND NORMAN S. THOMPSON

MAY, 1979

The reaction of tall oil fatty acids during simulated oxygen delignification

1. Effects of reaction variables

Gerald R. Mittet and Norman S. Thompson
The Institute of Paper Chemistry, Appleton, Wis. 54912

Keywords: tall oil; fatty acids; chemical degradation; delignification; oxygen; alkalis; oxygen pulping; process variables

ABSTRACT

The reactions of tall oil fatty acids and esters were investigated under conditions simulating those of oxygen-alkali delignification. A 2^5 half factorial experimental design covered the effects of temperature, reaction time, oxygen pressure, alkali, and substrate on the degradation of methyl oleate and methyl linoleate. Alkali had the most pronounced effect of these variables. In contrast to the behavior of carbohydrates and lignin, fatty acids and esters were relatively stable in oxygen-hydroxide, and were extensively oxidized in oxygen-bicarbonate. Those fatty acid esters which were not degraded by the oxygen and bicarbonate were not saponified and were not converted to water-soluble soaps. These results suggest that tall oil fatty acid recovery from oxygen-bicarbonate or oxygen-carbonate delignification will not be possible without some type of pretreatment. In reaction systems containing bicarbonate, wood exerted an apparent inhibition with regard to fatty acid autoxidation. More extensive degradation of the fatty acid esters occurred when wood meal was replaced with cotton linters. The protective effect of wood was lost or diminished by sodium hydroxide.

This paper has been submitted for publication in *Tappi*.

Introduction

Although oxygen-alkali pulping has been investigated as an alternative to kraft pulping, tall oil recovery has not been considered in that research. Tall oil is a valuable by-product which, if lost, would offset some of the benefits of oxygen-alkali pulping. The reactions of tall oil components during oxygen-alkali deliginification were discussed by Hrutfiord and Hopley (1) who compared soda with soda-oxygen pulping and found that inclusion of oxygen markedly reduced tall oil yield. Erickson and Dence (2), delignifying thermomechanical pulp with oxygen and hydroxide observed similar results. Pearl and Dickey (3) reported that some of the tall oil loss incurred during oxygen-alkali delignification of wood chips could be attributed to retention of fatty and resin acids in the washed pulp. The present investigation was undertaken to systematically examine and compare the effects of selected parameters on the reactions of tall oil fatty acids with oxygen and alkali under conditions simulating those of oxygen-alkali delignification.

Five reaction variables studied were reaction temperature, reaction time, oxygen pressure, alkali, and substrate. Arbitrarily chosen high and low levels, representing the probable extremes of an oxygen-alkali delignification process, were assigned to each variable. Those assignments, which are listed in Table I, were made on the assumption that changing any variable from its low level to its high level would increase fatty acid degradation. Only the reactions of fatty acids, which constitute one of the important fractions of crude tall oil, were examined.

[Table I here]

Besides time, temperature and oxygen pressure, alkali was included to determine if a bicarbonate- or hydroxide-based delignification system would be more conducive to recovery of the tall oil fatty acids. The substrate was varied to see if lignin would inhibit fatty acid oxidation. Since more extensive oxidation was expected when the lignin content was low, cotton linters was defined as the higher level of the substrate variable. Prior to each reaction, the substrate, either cotton or wood meal, was impregnated with a mixture of methyl oleate and methyl linoleate. We investigated the reactions of only these two compounds because oleic acid and linoleic acid are by far the two most important tall oil fatty acids (4).

[Chemical structure here]

Although fatty acids occur in wood primarily as triglyceride esters, we used methyl esters because we could readily procure and analyze them.

Because of the number of variables considered in the experimental program, we used a 2^5 half factorial experimental design (5). Sixteen different reactions were required to satisfy the design; each variable was assigned to its high level in exactly eight of them, and to its low level in the remaining eight. The complete half factorial experimental design is outlined in Table II.

[Table II here]

For any designated response, the half factorial design permits determination of five main effects, one for each variable, and the ten two-factor interactions between variables. A main effect is defined as the overall change in the response, averaged over all reactions, which occurs when a variable is raised from its lower level to its higher level.

The main effect of any specific variable is determined by calculating the average response of all those reactions which involve the variable only at its lower level, and subtracting that quantity from the average response of those reactions involving the variable only at its higher level. A two-factor interaction exists if the effect of one variable is dependent upon the level of another.

Three-factor interactions exist if the two-factor interaction between any two variables is dependent upon the level of a third variable. Similarly, a four-factor interaction exists when a three-factor interaction is dependent upon the level of a fourth variable. In a full factorial experimental design, all main effects and interactions may be determined unequivocally. However, the magnitudes of the higher order interactions are often negligibly small in comparison with the magnitudes of the main effects and two-factor interactions. In the half factorial design developed for this investigation, the four-factor interaction involving any four variables is equated with the main effect of the fifth variable. The three-factor interaction among any three variables is equated with the two-factor interaction between the other two. To determine the main effects and two-factor interactions, all three- and four-factor interactions are presumed to be zero.

To calculate main effects and interactions, suitable responses must be defined and measured for each reaction. In the present case, two responses, the total percent yields of unoxidized oleate and linoleate, were measured in each reaction. The total yields corresponded to the combined yields of methyl esters and free fatty acids measured for each component after each reaction. Two main effects, one for each response, were determined independently for each variable. Similarly, two separate two-factor interactions were calculated for each pair of variables.

Experimental

Wood meal was prepared by grinding loblolly pinewood chips in a Wiley mill to pass through a plate perforated with 1/8 inch diameter holes. The wood meal was extracted thoroughly with acetone to remove all naturally occurring tall oil components, washed successively with SO_2 water and distilled water to decrease its metal ion content, and then air dried. All oxidations were carried out in a 1-L stainless steel reaction vessel. Prior to each reaction, the fatty acid methyl esters (1.72 g methyl oleate and 2.12 g methyl linoleate) were dissolved in acetone and slurried with the substrate, which consisted of either wood meal (50 g) or cotton linters (30 g). Less cotton than wood was employed because of its greater water absorption. The acetone was then driven off by evaporation under reduced pressure, leaving the substrate impregnated with the fatty acid esters. The reaction vessel, containing 175 mL of distilled water, was preheated on a boiling water bath to 80°C. The alkali, either sodium hydroxide (11 g) or sodium bicarbonate (23.1 g), was then dissolved in the water, and that solution was mixed thoroughly with the ester-impregnated substrate, leaving a porous plug of alkali, water, substrate, and fatty acid esters. The reactor was then sealed, purged with oxygen, and pressurized to the nominal reaction pressure with oxygen. The charged reactor was immediately lowered into an oil bath which had been preheated to the predetermined reaction temperature, and measurement of the reaction time commenced. At the end of each reaction, the vessel was cooled in ice water and vented to atmospheric pressure. The alkaline reaction product was acidified with sulfuric acid and filtered on a coarse sintered glass funnel. The filtrate and the residual substrate were both extracted with ether for twenty-four hours in continuous extractors. The ether extracts were combined and fractionated into neutrals and weak acids as described by Zinkel and Rowe (6). The neutrals, which contained unsaponified fatty acid methyl esters, and the weak acids, containing free fatty acids, were analyzed by gas liquid chromatography on a 6-ft stainless steel column packed with 10% EGSS-X on 100/120 Gas Chrom P at a temperature of 170°C. The free fatty acids were first converted to methyl esters with diazomethane, and methyl eicosanoate internal standard was added to both fractions. The carrier gas was helium at a flow rate of 25 mL/min, and the gas chromatograph was equipped with a flame ionization detector.

Results and discussion

Results of the half factorial experimental design are presented in Tables III, IV and V. Listed in the first of those tables are the yields of unoxidized fatty acid methyl esters, free fatty acids, and their total combined yields. We used total yields for calculating main effects and interactions. In general, methyl linoleate was degraded considerably more than methyl oleate, as was expected (7). The first step of fatty acid autoxidation (oxidation by molecular oxygen) is abstraction of a hydrogen atom and formation of a free radical. In unsaturated compounds, allylic hydrogen atoms bonded to carbon atoms adjacent to the double bonds are abstracted preferentially. Methyl oleate contains two reactive sites, located on either side of the double bond, while methyl linoleate contains a particularly reactive "activated" methylene group between the two double bonds. Because of the ease with which a hydrogen atom is abstracted from that methylene unit, methyl linoleate undergoes autoxidation more rapidly than methyl oleate.

[Tables III, IV and V here]

The main effects of all variables, and all of their two-factor interactions, are presented in Tables IV and V. Listed in Table IV are the main effects and interactions related only to the total yield of oleate, while the effects and interactions shown in Table V relate only to the total yield of linoleate. Included in each table is an analysis of variance to determine which effects and interactions may be considered significant. The significance of each main effect and interaction is tested by comparing its mean square with an error mean square term derived from the results of reactions 17-21. If the probability that an observed main effect of interaction results from experimental error is less than 1%, then the effect or interaction is considered highly significant, as indicated by a double asterisk (**). If that probability is greater than 1% and less than 5%, then the effect of interaction is considered significant and is so designated by a single asterisk (*). Other effects or interactions are considered possibly significant, with less than a 10% error probability, if their F-tests exceed 5.54.

Almost all of the main effects are significant or highly significant. The main effect of temperature related to the yield of linoleate is probably significant, although its F-test falls slightly below the 5% level. Although the main effect of substrate related to the yield of oleate is not itself significant, the substrate did interact significantly with both pressure and alkali. All of the main effects possess negative signs, which shows that raising any variable from its low level to its high level decreases the yields of oleate and linoleate. Alkali is the most influential variable. Substituting sodium bicarbonate for sodium hydroxide decreased the average yields of oleate and linoleate by more than 30%.

The main effect of substrate is also negative, indicating that fatty acid yields decrease if cotton is substituted for wood. Substrate is, however, involved in two significant interactions. The pressure-substrate interaction has a positive sign, showing that the effect of pressure is more pronounced at the lower level of substrate and that the effect of substrate is greater at the lower level of pressure. In the presence of wood meal, higher oxygen pressure causes substantial decreases in fatty acid yields. Conversely, wood exhibits a "protective effect" toward fatty acid autoxidation at high pressure. On the other hand, oxygen pressure does not influence fatty acid oxidation in the presence of cotton.

The alkali-substrate interaction has a negative sign and a relatively large magnitude. The effect of alkali is greater in the presence of cotton, therefore, than in the presence of wood. However, in either system, replacing hydroxide with bicarbonate results in decreased yields of both oleate and linoleate. On the other hand, while wood meal inhibits fatty acid oxidation in the presence of bicarbonate, the substrate effect is reversed in the presence of hydroxide. When hydroxide is used, substituting cotton for wood meal results in an average increase in the yields of oleate and linoleate, which is the opposite of what is found with bicarbonate.

The inhibitory effect of wood on fatty acid oxidation may result from oxygen diffusivity limitations, as indicated by the pressure-substrate interaction, or it may derive from the antioxidant characteristics of lignin-derived phenols. Phenolic antioxidants are used to effectively retard the autoxidation of fats and oils (8), and the presence of phenols in oxygen-alkali spent liquor has been demonstrated (9). Those phenols might lose their antioxidant properties when ionized, which could account in part for the alkali-substrate interaction. The phenols exist in their unionized states in the presence of bicarbonate and are ionized by hydroxide. On the other hand, the alkali-substrate interaction may reflect the rapid and extensive pH drop which occurs when wood reacts with oxygen and sodium hydroxide. As indicated by the high magnitude of the alkali main effect, the fatty acids should be autoxidized more rapidly as the pH drops. A less dramatic pH drop is expected in the cotton-hydroxide system. Therefore, the high magnitude of the alkali effect in the presence of cotton alone suggests a very large pH differential between the bicarbonate- and hydroxide-based reactions. That pH differential is diminished in the presence of wood, and the alkali effect subsequently decreases. The beneficial effect of wood in systems containing hydroxide might be overwhelmed by an effect resulting from the decrease in pH which occurs as the hydroxide is consumed.

The effect of alkali on the oxidation of fatty acids contrasts with its effect on the autoxidation of carbohydrates and lignin. Degradation of the latter substances is promoted by hydroxide, while degradation of the fatty acids is promoted by bicarbonate. However, as examination of the results in Table III will show, the fatty acid esters were saponified by the hydroxide and not by the bicarbonate. To insure that the alkali effect did not reflect differences in the reactivity between fatty acid methyl esters and fatty acid soaps, two additional oxidations of free fatty acids were conducted under differing alkali conditions. The reaction conditions and yields of unoxidized starting material are shown in Table VI.

[Table VI here]

Consistent with the results observed during the oxidations of fatty acid methyl esters, the free fatty acids underwent much more extensive degradation in the presence of sodium bicarbonate. The enhanced reactivity of the fatty acids and their derivatives in the presence of bicarbonate may in part be due to the formation of carbonate radicals created during reactions between hydroxyl radicals and carbonate or bicarbonate ions (10). In systems containing large quantities of bicarbonate or carbonate, relatively high steady state concentrations of those radicals might be attained, and they might initiate fatty acid autoxidation. The hydroxyl radicals themselves can initiate fatty acid oxidation, and those highly reactive radicals could interact directly with the substrate to a greater extent than the carbonate radicals. The participation of carbonate radicals in the oxidation reactions is only speculated, since not enough information is available to understand the alkali effect.

Conclusions

1. Although unsaturated tall oil fatty acids and their esters autoxidize during oxygen-alkali delignification, degradation of the acids is not complete except under very severe reaction conditions. Tall oil fatty acid recovery may be compatible with oxygen-alkali delignification.

2. Alkali is the most critical variable affecting reactions of the tall oil fatty acids. The fatty acids and their esters were much more extensively degraded in the presence of bicarbonate than they were with hydroxide under otherwise identical reaction conditions. This behavior, which is the opposite of that observed for carbohydrates or lignin, may result from the accumulation of carbonate radicals in the reaction system. Furthermore, those fatty acid esters which did survive treatment with oxygen and bicarbonate were not saponified, and they could not be washed from pulp with water. Recovery of tall oil fatty acids will probably be eliminated in an oxygen-alkali delignification process which utilizes bicarbonate or carbonate exclusively.

3. When bicarbonate was used, the fatty acid esters were more stable in the presence of wood meal than in the presence of cotton linters. This stability did not occur when sodium hydroxide was used.

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I. Reaction variables

Variable	Low level	High level
Temperature, °C	100	160
Reaction, time, hr	2	8
Oxygen pressure[a], kPa	690	3500
Alkali[b]	11 g NaOH	23.1 g $NaHCO_3$
Substrate[c]	50 g wood meal	30 g cotton linters

[a] 6.9 kiloPascals = 1.0 psi. [b] The alkali charge in all reactions was 17%, as Na_2O, based on o.d. wood. [c] All reactions were conducted at high consistency.

II. Half factorial design for oxidations of fatty acid methyl esters

Reaction no.	Temp., °C	Reaction time, hr	O_2 Pressure, kPa	Alkali	Substrate
1	100	2	690	NaOH	Cotton
2	160	2	690	NaOH	Wood
3	100	8	690	NaOH	Wood
4	160	8	690	NaOH	Cotton
5	100	2	3500	NaOH	Wood
6	160	2	3500	NaOH	Cotton
7	100	8	3500	NaOH	Cotton
8	160	8	3500	NaOH	Wood
9	100	2	690	$NaHCO_3$	Wood
10	160	2	690	$NaHCO_3$	Cotton
11	100	8	690	$NaHCO_3$	Cotton
12	160	8	690	$NaHCO_3$	Wood
13	100	2	3500	$NaHCO_3$	Cotton
14	160	2	3500	$NaHCO_3$	Wood
15	100	8	3500	$NaHCO_3$	Wood
16	160	8	3500	$NaHCO_3$	Cotton
17[a]	130	5	2100	NaOH	Wood
18[a]	130	5	2100	NaOH	Wood
19[a]	130	5	2100	NaOH	Wood
20[a]	130	5	2100	$NaHCO_3$	Wood
21[a]	130	5	2100	$NaHCO_3$	Wood

[a] Reactions 17-21 were not part of the actual half factorial design and were included for estimation of experimental error.

III. Yields of unoxidized oleate and linoleate

Reaction no.	Yield of starting material[a] (g, as methyl esters)						Total yield, %	
	Methyl esters		Free fatty acids		Total			
	Oleate	Linoleate	Oleate	Linoleate	Oleate	Linoleate	Oleate	Linoleate
1	0.01	0.01	1.49	1.58	1.50	1.59	87.2	75.0
2	0.10	0.05	1.28	1.31	1.38	1.36	80.2	64.2
3	0.08	0.06	1.30	1.43	1.38	1.49	80.2	70.3
4	0	0	1.39	1.05	1.39	1.05	80.8	49.5
5	0.28	0.22	0.94	1.05	1.22	1.27	70.9	59.9
6	0	0	1.27	0.98	1.27	0.98	73.8	46.2
7	0	0	1.39	1.38	1.39	1.38	80.8	65.6
8	0.08	0.02	0.46	0.30	0.54	0.32	31.4	15.1
9	1.37	1.31	0.02	0.02	1.39	1.33	80.8	62.7
10	0.36	0.28	0.02	0.01	0.38	0.29	22.1	13.7
11	0.39	0.02	0.02	0.01	0.41	0.03	23.8	1.4
12	0.77	0.73	0.09	0.10	0.86	0.83	50.0	39.2
13	1.03	0.20	0.02	0	1.05	0.20	61.0	9.4
14	0.53	0.84	0.02	0.02	0.55	0.86	32.0	40.6
15	0.77	0.49	0.02	0.01	0.79	0.50	45.9	23.6
16	0.16	0.08	0.02	0.02	0.18	0.10	10.5	4.7
17[b]	0.33	0.16	0.60	0.58	0.93	0.74	54.1	34.9
18[b]	0.12	0.05	1.06	1.06	1.18	1.11	68.6	52.4
19[b]	0.29	0.12	0.84	0.93	1.13	1.05	65.7	49.5
20[b]	0.69	0.64	0.01	0.01	0.70	0.65	40.7	30.7
21[b]	0.78	0.70	0.01	0.01	0.79	0.71	45.9	33.5

[a] All reaction systems initially contained 1.72 g methyl oleate and 2.12 g methyl linoleate. [b] Reactions 17-21 were not part of the half factorial experimental design (reactions 1-16), but were included for estimation of error.

IV. Main effects and two-factor interactions related to the total yield of oleate

Main effect	Degrees of freedom	Sum of squares	Mean square	F-Test (mean sq/EMS)	Sign and magnitude of effect or interaction
Temperature	1	1402.5	1402.5	32.09*	-18.7*
Reaction time	1	683.8	683.8	15.65*	-13.1*
Oxygen pressure	1	610.1	610.1	13.96*	-12.4*
Alkali	1	4199.0	4199.0	96.09**	-32.4**
Substrate	1	61.6	61.6	1.41	-3.9
Interaction					
Temperature-time	1	71.4	71.4	1.63	+4.2
Temperature-pressure	1	324.0	324.0	7.41	-9.0
Temperature-alkali	1	121.0	121.0	2.77	-5.5
Temperature-substrate	1	21.6	21.6	0.49	+2.3
Time-pressure	1	70.6	70.6	1.62	-4.2
Time-alkali	1	44.9	44.9	1.03	-3.4
Time-substrate	1	4.2	4.2	0.10	+1.0
Pressure-alkali	1	122.1	122.1	2.79	+5.5
Pressure-substrate	1	948.6	948.6	21.71*	+15.4*
Alkali-substrate	1	1428.8	1428.8	32.70*	-18.9*
Error estimate					
Reactions 17-19	2	117.7	(Sums of squares about the means)		
Reactions 20-21	1	13.5			
Reactions 17-21	3	131.2	43.7 = Error mean square (EMS)		

---

[a] The significance levels of the F-test are 5.54 at the 10% level, 10.1 at the 5% level and 34.1 at the 1% level. An effect or interaction is considered highly significant (**) if its mean square exceeds 1490.2, significant (*) if its mean square is between 441.4 and 1490.2, and possibly significant if its mean square is below 441.4 but greater than 242.1.

V. Main effects and two-factor interactions related to the total yield of linoleate

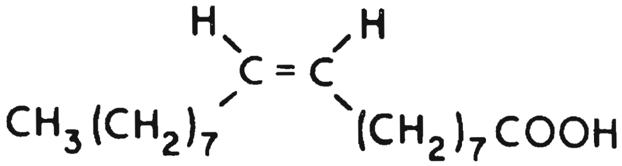
Main effect	Degrees of freedom	Sum of squares	Mean square	F-Test (mean sq/EMS)	Sign and magnitude of effect or interaction
Temperature	1	560.5	560.5	9.42	-11.8
Reaction time	1	654.1	654.1	10.99*	-12.8*
Oxygen pressure	1	768.7	768.7	12.92*	-13.9*
Alkali	1	3921.9	3921.9	65.91**	-31.3**
Substrate	1	757.6	757.6	12.73*	-13.8*
Interaction					
Temperature-time	1	6.4	6.4	0.11	-1.3
Temperature-pressure	1	5.2	5.2	0.09	-1.1
Temperature-alkali	1	586.9	586.9	9.86	+12.1
Temperature-substrate	1	25.3	25.3	0.43	+2.5
Time-pressure	1	4.1	4.1	0.07	+1.0
Time-alkali	1	10.1	10.1	0.17	-1.6
Time-substrate	1	196.7	196.7	3.31	+7.0
Pressure-alkali	1	70.1	70.1	1.18	+4.2
Pressure-substrate	1	435.8	435.8	7.32	+10.4
Alkali-substrate	1	1674.9	1674.9	28.15*	-20.5*
Error estimate					
Reactions 17-19	2	175.9	(Sums of squares about the means)		
Reactions 20-21	1	3.9			
Reactions 17-21	3	179.8	59.5 = Error mean square (EMS)		

[a] The significance levels of the F-test are 5.54 at the 10% level, 10.1 at the 5% level and 34.1 at the 1% level. An effect or interaction is considered highly significant (**) if its mean square exceeds 2029.0, significant (*) if its mean square is between 601.0 and 2029.0, and possibly significant if its mean square is below 601.0 but greater than 329.6.

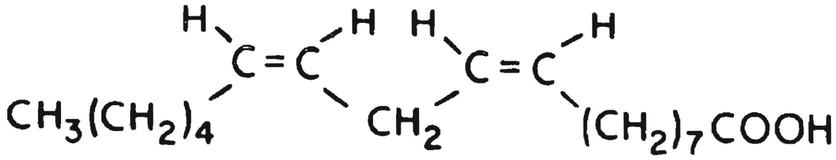
VI. Oxidations of free fatty acids[a]

			Weights of fatty acids, g				Yields of fatty acids, %	
			Starting material		Reaction product			
Reaction no.	Alkali	Substrate	Oleic	Linoleic	Oleic	Linoleic	Oleic	Linoleic
22	NaOH	Cotton	1.54	2.23	1.34	1.47	87.0	65.9
23	$NaHCO_3$	Cotton	1.54	2.23	0.19	0.01	12.3	0.4

[a] Both reactions were conducted at 130°C for 5 hours under an initial oxygen pressure of 2100 kPa.



oleic acid



linoleic acid

attachment 12, section 9.

The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

The Degradation of Tall Oil Fatty Acids by Molecular Oxygen in Alkaline Media

Gerald R. Mittet

January, 1979

THE DEGRADATION OF TALL OIL FATTY ACIDS BY MOLECULAR OXYGEN IN ALKALINE MEDIA

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SUMMARY

The reactions of tall oil fatty acids and their esters with molecular oxygen and alkali were investigated under conditions chosen to simulate those which might be encountered in an oxygen-alkali delignification process. The primary objective of the investigation was to determine those reaction conditions most compatible with recovery of the fatty acids. Another objective, complementary to the first, involved identification of the fatty acid oxidation products and measurements of their yields. The product analyses were intended to account for the fatty acid losses which did occur, and to obtain some understanding of the fatty acid oxidation mechanisms.

To satisfy the primary objective, a half factorial experimental design involving sixteen reactions was developed to investigate the relative effects of five variables on the degradation of two fatty acid esters, methyl oleate and methyl linoleate. The variables considered were temperature, reaction time, oxygen pressure, alkali and substrate. The magnitudes of the first three parameters were varied, while the alkali variable was represented by either sodium hydroxide or an equimolar amount of sodium bicarbonate. The substrate variable, which consisted of either preextracted loblolly pinewood meal or cotton linters, was included to investigate the "protective effect" of wood on oxidation of the fatty acid esters. The two substrates differed most significantly in their lignin contents, since the protective effect was interpreted as a possible antioxidant property of lignin derived phenols.

To facilitate identification of fatty acid oxidation products, the methyl esters and sodium soaps of pure oleic acid and linoleic acid were oxidized. Their reaction products were analyzed by combined gas chromatography-mass spectrometry. The reactions of four saturated fatty acids possessing from sixteen to twenty-two carbon atoms were also briefly investigated.

However, the saturated fatty acids and their esters were very resistant to reaction with oxygen-alkali, and none of their oxidation products were detected.

Effects of the reaction variables on fatty acid degradation were determined from the yields of unreacted starting material measured in all reactions associated with the half factorial experimental design. Raising the temperature from 100 to 160°C increased oxidation of the fatty acid esters to about the same extent as extending the reaction time from 2 to 8 hours. Increasing the oxygen pressure from 690 to 3500 kPa also resulted in more extensive fatty acid oxidation. However, the effect of this variable was dependent on the nature of the substrate. Although oxygen pressure had a significant effect in reaction systems containing wood meal, its effect was negligible in systems containing cotton linters. Alkali exerted by far the most pronounced effect of any variable considered. Much more extensive degradation of both fatty acid methyl esters and free fatty acids was promoted by the weaker base, sodium bicarbonate. The possible participation of carbonate radicals was considered to explain the observed result. The effect of substrate was markedly influenced by the alkali. Wood meal did exhibit a protective effect when fatty acids or their esters underwent reaction with sodium bicarbonate and oxygen, and that effect was lost when the bicarbonate was replaced with hydroxide.

Distributions of the fatty acid oxidation products were also dependent upon the reaction conditions. The identified oxidation products generally accounted for between 30 and 40% of the starting material consumed. However, small quantities of numerous other compounds were detected by gas-liquid chromatography. The remainder of the lost matter was assumed to consist of those compounds and other low molecular weight oxidation products. Carboxylic acids, dicarboxylic acids and long chain hydroxy acids were found among the products of almost all reactions. α-Hydroxy mono- and dibasic-carboxylic acids were other major products, but only of reactions conducted in aqueous sodium hydroxide solutions, or carried out in the presence of both sodium hydroxide and cotton linters. Formation of the α-hydroxy acids was therefore promoted by strong alkali. Those compounds were not significant products of any reactions conducted with sodium bicarbonate, nor were they formed in appreciable quantities if the reaction system contained wood meal and sodium hydroxide. Other important compounds found among the products of all sodium bicarbonate based reactions were ω-hydroxy acids. The oxidation reactions were more selective at low temperature than at high temperature. Cleavage of the fatty acid molecules at or near the locations of their double bonds was preferred at 100°C, while complex mixtures of reaction products containing many low molecular weight compounds were obtained at 160°C. Hydroperoxides were not identified; such compounds were the presumed primary products of fatty acid autoxidation. Different hydroperoxide decomposition pathways were considered to account for formation of the observed products. Several intermediate reaction products were identified which provided additional evidence for the reaction mechanisms suggested.

The results of this investigation indicate that recovery of tall oil fatty acids will not be possible in an oxygen-bicarbonate delignification process without some type of pretreatment, such as alkaline extraction. Although the naturally occurring fatty acid esters will not be saponified in systems containing oxygen and bicarbonate, they are likely to undergo extensive oxidation degradation. Conditions most favorable to fatty acid recovery during oxygen-alkali delignification include low temperature, short reaction time and strong alkali; a high pH should be maintained if recovery of the fatty acids is desired. Oxidation of the fatty acids and their esters results in the formation of many potentially valuable acidic oxidation products; yields of individual compounds are generally very low, and their recovery from spent liquor would be difficult.

THESIS OBJECTIVES

This thesis was conceived to investigate the reactions of tall oil fatty acids under conditions simulating those of oxygen-alkali delignification. The methyl esters or sodium soaps of oleic acid, linoleic acid and several saturated fatty acids were the compounds investigated.

An experimental program designed to determine the effects of temperature, reaction time, oxygen pressure, alkali, and lignin content on the autoxidation of methyl oleate and methyl linoleate was developed. The primary purpose of the program was to define conditions least likely to promote degradation of tall oil fatty acids during delignification of wood or pulp with oxygen and alkali.

Another important goal of the experimental program was to account for the losses of the fatty acid esters which did occur. This objective required identification of fatty acid oxidation products and measurements of their yields. This phase of the investigation was intended to explore the possibility of recovering potentially valuable oxidation products and to clarify the mechanism of fatty acid degradation by oxygen and alkali.

INTRODUCTION

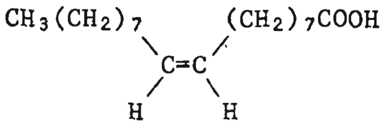
Because of environmental problems associated with the kraft pulping process, alternate pulping methods have been devised. One of the more promising alternatives is delignification with oxygen and alkali. However, the viability of tall oil and turpentine recovery, which is an important advantage of the kraft process, has not been adequately explored in research on oxygen-alkali delignification.

Among the extractives of wood, three classes of compounds comprise the commercially important by-products of kraft pulping. They are monoterpenes, diterpene resin acids, and fatty acids. Monoterpenes constitute the major fraction of sulfate turpentine, while the resin and fatty acids are recovered from kraft black liquor as tall oil soap. The probable reactions of extractives during oxygen-alkali delignification were discussed by Hrutfiord and Hopley (1). They predicted that autoxidation of the extractive components would result in decreased yields of both tall oil and turpentine. Tall oil yields from thermomechanical pulp treated with oxygen and sodium hydroxide were measured by Erickson and Dence (2), while Pearl and Dickey (3) compared the yields of tall oil obtained after kraft, soda and soda-oxygen pulping of pinewood chips. In each case tall oil recovery after treatment with oxygen was substantially reduced from that which could be achieved by the kraft process. Presumably, the fatty and resin acids underwent oxidative degradation during delignification. However, Pearl and Dickey (3) also demonstrated that considerable quantities of tall oil components remained in soda and soda-oxygen pulps after they were washed with water. Similarly, Pusa and Virkola (4) found that substantial quantities of extractives remained in sulfite pulp after treatment with oxygen and sodium hydroxide.

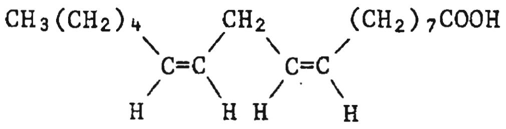
Evidence suggests that tall oil acids are at least partially degraded by oxygen and alkali. No attempts have been made to determine the conditions of oxygen-alkali delignification which might be most conducive to tall oil recovery. Furthermore, no satisfactory account has yet been made of the tall oil components which are consumed during delignification. This thesis, which is concerned specifically with the reactions of tall oil fatty acids, addresses both of those questions.

FATTY ACIDS OF SOUTHERN PINEWOOD

Tall oil fatty acids occur in wood predominately as triglyceride esters, with lesser quantities as sterol esters or waxes. The two most abundant fatty acids are oleic acid (cis-9-octadecenoic acid) and linoleic acid (cis,cis-9,12-octadecadienoic acid). In loblolly pinewood these two unsaturated compounds are found in approximately equal quantities and together account for about 80% of all the fatty acids (5). The third most abundant fatty acid is palmitic acid (hexadecanoic acid), a saturated acid which accounts for about 6% of all fatty acids in loblolly pine. The remaining fatty acids are saturated and unsaturated compounds of varying chain lengths and varying degrees of unsaturation.



Oleic Acid



Linoleic Acid

$CH_3(CH_2)_{14}COOH$

Palmitic Acid

AUTOXIDATION OF FATTY ACIDS

All of the fatty acids found in wood are susceptible to reactions with the molecular oxygen present in air; under ambient conditions such reactions are commonly termed autoxidations. Hereafter, autoxidation will refer to any reaction involving molecular oxygen. Olefin autoxidation was the subject of extensive research conducted under the direction of the British Rubber Producers Research Association. The kinetics and mechanism of autoxidation were elucidated during those investigations, and the results have been discussed in reviews by Bolland (6) and by Bateman (7). The mechanism of autoxidation which was proposed at that time, and which is still generally accepted, is represented by Equations (1) through (6).

$$
\begin{array}{lllr}
\text{Initiation} & RH + I\ (\text{Initiator}) & \longrightarrow R\cdot + IH & (1)\\
\text{Propagation} & R\cdot + O_2 & \longrightarrow ROO\cdot & (2)\\
 & ROO\cdot + RH & \longrightarrow ROOH + R\cdot & (3)\\
 & R\cdot + R\cdot & \longrightarrow \text{"Inert"} & (4)\\
\text{Termination} & R\cdot + ROO\cdot & \longrightarrow \text{Products} & (5)\\
 & ROO\cdot + ROO\cdot & \longrightarrow & (6)
\end{array}
$$

The mechanism outlined is a radical chain reaction. Autoxidation may be initiated by any species which will induce cleavage of carbon-hydrogen bonds. Common initiators include free radicals and ultraviolet light. In the first step of the sequence a hydrogen atom is abstracted by the initiating species, yielding a chain-propagating free radical (R•). An allylic hydrogen atom is usually abstracted preferentially from unsaturated compounds, since the resulting free radical is resonance-stabilized. The free radical rapidly combines with oxygen to produce a peroxy radical as shown in Equation (2). The peroxy radical abstracts a hydrogen atom from a second reactant molecule, yielding another reactive free radical and a hydroperoxide, as represented by Equation (3). Reactions (2) and (3) are defined as chain-propagating steps, since in each case a radical is formed which may directly or indirectly initiate further oxidation. Under mild conditions hydroperoxides are the end products of autoxidation, which is terminated when the free radicals decompose to form products incapable of initiating or propagating further reaction, as indicated by

Equations (4)-(6). For autoxidation, the chain length is defined as the number of times Reactions (2) and (3) will occur before the sequence is interrupted by a termination reaction. At relatively high oxygen pressures the rates of the termination steps, (4) and (5), become insignificant compared to the rate of propagation step, (3), and termination occurs almost exclusively by Reaction (6). Under suitable reaction conditions, and in the absence of pro- or antioxidants, autoxidation may be characterized by long chain lengths and high yields of hydroperoxides.

The autoxidation of fatty acids and fatty acid derivatives may also be described by the general mechanism of autoxidation shown in Equations (1) through (6). In fact, esters of oleic acid and linoleic acid were commonly used as model compounds in many of the studies dealing with general olefin autoxidation. Numerous investigations by many different groups of workers have been directed specifically to the autoxidation reactions of fats and oils. Most of this work was undertaken to clarify the chemistry associated with the development of rancidity in cooking oils and the polymerization of drying oils. In most instances, the initial stages of autoxidation were adequately described by the radical chain mechanism. Research dealing with the autoxidation of fats and oils has been reviewed by Holman (8), Swern, *et al.* (9), and Swern and Coleman (10).

METHYL PALMITATE

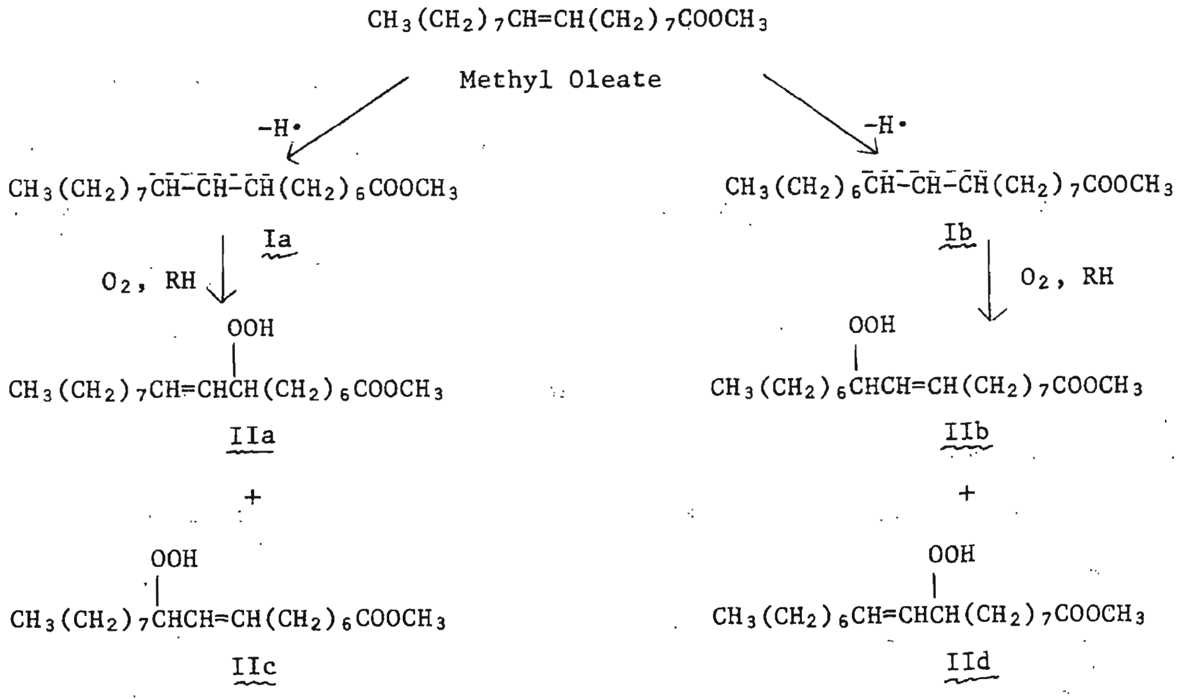
While all fatty acids are subject to reaction with oxygen, saturated fatty acids are autoxidized very slowly unless relatively severe conditions are imposed. Since such compounds do not contain double bonds, the oxidations are not as specific as analogous reactions involving unsaturated compounds. Hydroperoxide formation during autoxidation of methyl palmitate was investigated by Brodnitz, et al. (11). The ester was heated to 150°C in air, and an analysis of the

$$\underset{\text{Methyl Palmitate}}{CH_3(CH_2)_{14}COOCH_3} \xrightarrow{O_2} \text{Numerous Monohydroperoxides}$$

resulting mixture of hydroperoxides was attempted. The results indicated that monohydroperoxides were the primary products. Although oxidation appeared to occur preferentially toward the center of the molecule, the initial attack by oxygen was not favored at any particular site.

METHYL OLEATE

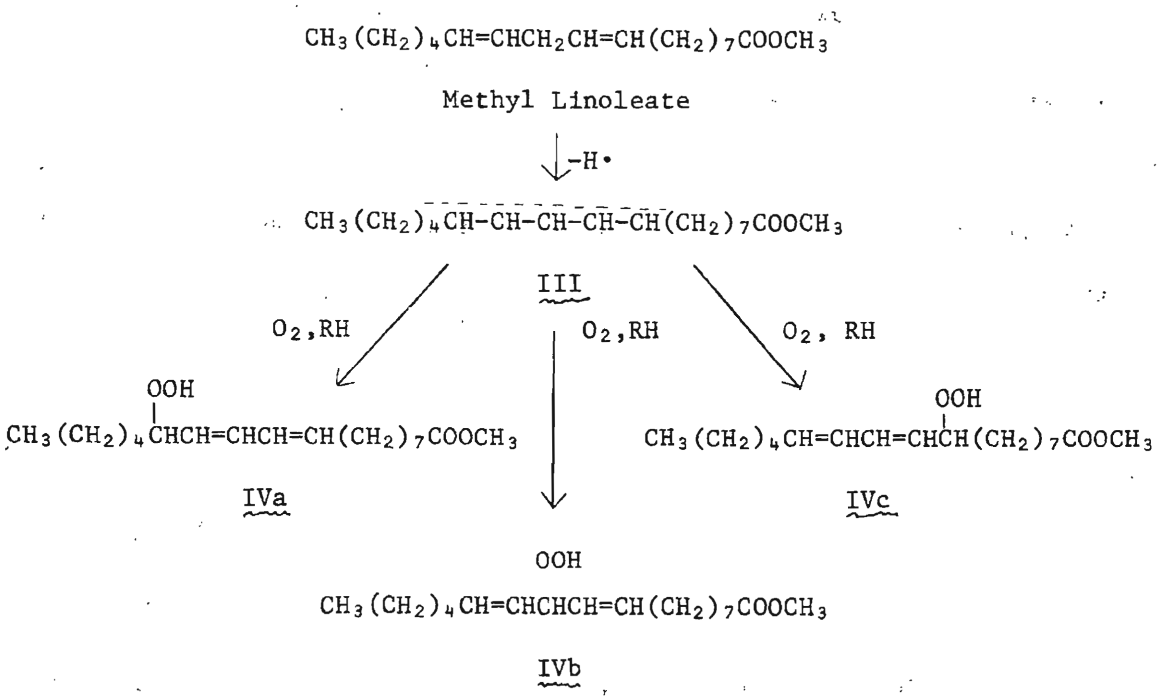
Methyl oleate possesses two allylic methylene groups, either one of which may lose a hydrogen atom to an initiating free radical. Two different resonance-stabilized allylic free radicals may thus be formed (Ia, Ib), and each of them may combine with oxygen at two different sites. In methyl oleate, hydroperoxide



formation may occur at any one of the four carbon atoms part of, or adjacent to, the original double bond. Furthermore, each of the four probable hydroperoxides, the general structures of which are shown (IIa-IId), has two geometric isomers. Structural determinations of the hydroperoxides obtained from autoxidized methyl oleate have been the objects of several recent investigations (12-14). Although this aspect of autoxidation was also of considerable interest in earlier work (8-10), analytical techniques had not been developed which permitted unequivocal identifications of individual hydroperoxides. All eight of the predicted hydroperoxides were identified by Garwood *et al.* (12) when methyl oleate was autoxidized at temperatures ranging from 25 to 75°C. The four positional isomers were found in approximately equal quantities at all temperatures. However, the hydroperoxides tended to assume *trans* configurations, particularly in those compounds (**IIb**,**IId**) whose formation coincided with migration of the double bond. Similar results were reported by Capella, Piretti and coworkers (13,14).

METHYL LINOLEATE

Unlike methyl oleate, methyl linoleate possesses one activated methylene group which is particularly susceptible to hydrogen atom abstraction. Removal of a hydrogen atom from the activated methylene unit, which is located between the two unconjugated double bonds of the molecule, yields a free radical (**III**) which is resonance stabilized over five carbon atoms. The attack on methyl linoleate by oxygen may conceivably occur at any one of three sites, as illustrated. Furthermore, each of the three possible positional hydroperoxide isomers (**IVa**-**IVc**) has four potential geometric isomers. However, results from early work by Privett, *et al.* (15) and Cannon, *et al.* (16) indicated that the hydroperoxides initially formed during autoxidation of methyl linoleate were predominately conjugated dienes possessing *cis*-*trans* configurations. Those compounds were apparently capable of undergoing rearrangements to the conjugated



trans-*trans* isomers. At most, only very small quantities of the unconjugated hydroperoxide (IVb) were formed, although Khan, *et al.* (17) obtained indirect evidence which suggested that the latter isomer was also produced to some extent. More recently, Chan and Levett (18) detected only four hydroperoxides after autoxidation of methyl linoleate. They were the *cis*-*trans* and *trans*-*trans* isomers of the conjugated hydroperoxides IVa and IVc. In the *cis*-*trans* isomers the *trans* double bonds were located adjacent to the hydroperoxy groups. Schauenstein (19) investigated the autoxidation of methyl linoleate in dilute aqueous suspensions. Even when the fatty acid esters were dispersed in water the classical mechanism of autoxidation was apparently valid. The same hydroperoxides formed during conventional autoxidations were detected in the aqueous system.

PROOXIDANTS, ANTIOXIDANTS AND SYNERGISTS

Autoxidation is autocatalytic; the hydroperoxide primary products readily cleave to radical fragments which may initiate or propagate the chain reaction. Hydroperoxides may decompose either unimolecularly or bimolecularly, as shown by Equations (7) and (8).

$$ROOH \longrightarrow RO\cdot + HO\cdot \qquad (7)$$

$$2ROOH \longrightarrow ROO\cdot + RO\cdot + H_2O \qquad (8)$$

High hydroperoxide concentrations coupled with low temperatures favor the latter reaction, while high temperatures promote the unimolecular pathway (7).

Substances which increase the rate of autoxidation are termed prooxidants. Most prooxidants catalyze the decomposition of hydroperoxides and peroxides to free radicals capable of initiating or propagating the autoxidation reaction. Conversely, substances which inhibit autoxidation are termed antioxidants. Most antioxidants react with radicals and transform them to "inert" nonradical products, while others directly decompose hydroperoxides or peroxides to nonradical species. Compounds which enhance the effect of other antioxidants are called synergists; such substances may or may not possess antioxidant properties of their own. Prooxidation, antioxidation and synergism are all discussed in reviews by Ingold (20,21).

PROOXIDANTS

Autoxidation catalysis by transition metal ions is a well known example of prooxidation. The important reactions catalyzed by metal ions are shown by Equations (9) and (10).

$$M^{n+} + ROOH \longrightarrow M^{(n+1)+} + RO\cdot + HO^- \quad (9)$$

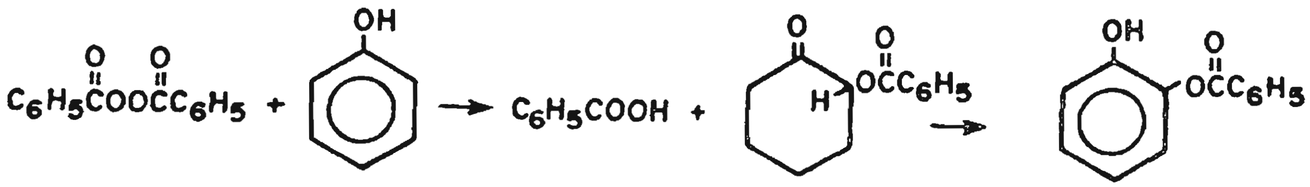
$$M^{(n+1)+} + ROOH \longrightarrow M^{n+} + ROO\cdot + H^+ \quad (10)$$

One reaction (9) corresponds to oxidation of a hydroperoxide to an alkoxy radical (RO•), while the other (10) represents reduction of a hydroperoxide to a peroxy radical (ROO•). Some metals promote both reactions and are true catalysts. In such cases the net reaction is the same as that represented by Equation (8).

Any other species which can promote the homolytic decomposition of hydroperoxides is a potential prooxidant. Free fatty acids undergo autoxidation more rapidly than fatty acid esters, presumably because the carboxyl groups complex with the hydroperoxides and catalyze their decomposition to free radicals (8,22). In the limiting case, catalytic influences of prooxidants are so effective that the rate of hydroperoxide decomposition approaches, or even attains, the rate of hydroperoxide production, and the autoxidation reaction loses its chain character. The maximum rate of autoxidation, limited only by the rates of Reactions (3) and (6), should then show a second order dependence on fatty acid ester concentration (7).

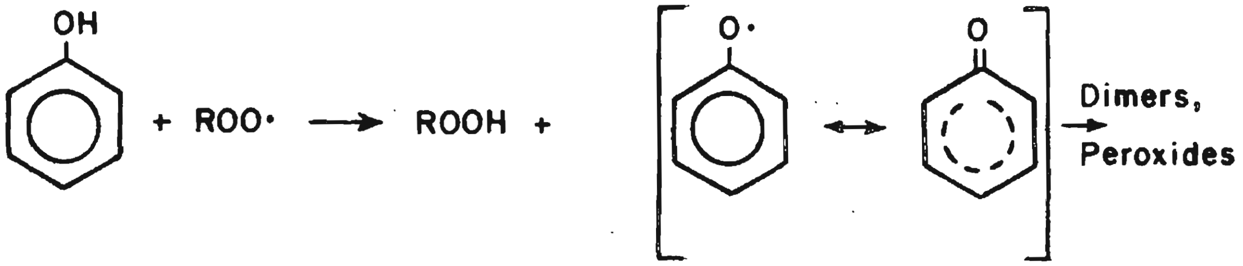
ANTIOXIDANTS

Among the most common antioxidants are phenolic compounds. In some instances phenols may convert peroxides directly to nonradical products. Denney and Denney (23) showed that phenol undergoes a reaction with benzoyl peroxide yielding benzoic acid and catechol monobenzoate, as shown below:



Similar reactions involving hydroperoxides were postulated by Ingold (20).

Phenols may also react with the radical decomposition products of peroxides and hydroperoxides, converting them to products which will not participate in autoxidation. The phenoxy radicals which are created tend to couple with other radicals rather than initiate autoxidation:



SYNERGISTS

The exact mechanism of synergism is not clear, but several possible effects of synergists have been considered (20). They may decompose or deactivate the hydroperoxides formed during reactions between radicals and antioxidants, or they may counteract the prooxidant tendencies of some antioxidants. For example, citric acid, a synergist, suppresses the hydroperoxide decompositions by phenolic antioxidants which would otherwise result in free radical formation.

AUTOXIDATION IN ALKALINE MEDIA

Autoxidation in alkaline media has also been the subject of extensive investigation. Much of the research in this area has been covered in reviews by Russell, et al. (24,25) and Sosnovsky and Zaret (26). All compounds which form carbanions are susceptible to autoxidation in basic systems. These include many hydrocarbons, aldehydes, ketones, esters and anhydrides. The mechanism of base catalyzed autoxidation, which is summarized by Equations (11) through (20), is similar to that previously described for normal olefin autoxidation.

Ionization	$RH + B^- \longrightarrow R^- + BH$		(11)
Initiation	$R^- + O_2 \longrightarrow R\cdot + O_2\cdot^-$		(12)
	$R^- + O_2\cdot^- \longrightarrow R\cdot + O_2^{-2}$		(13)
	$R^- + A \longrightarrow R\cdot + A\cdot^-$		(14)
Propagation	$R\cdot + O_2 \longrightarrow ROO\cdot$		(15)
	$ROO\cdot + R^- \longrightarrow ROO^- + R\cdot$		(16)
	$A\cdot^- + O_2 \longrightarrow A + O_2\cdot^-$		(17)
Termination	$R\cdot + O_2\cdot^- \longrightarrow ROO^-$		(18)
	$ROO\cdot + O_2\cdot^- \longrightarrow ROO^- + O_2$		(19)
	$2ROO\cdot \longrightarrow$ "Inert" Products		(20)

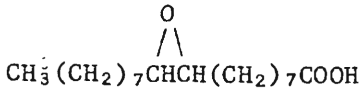
The initial step of autoxidation in basic media is formation of a carbanion (R^-). For very weakly acidic compounds this may be the rate limiting step. The carbanion then loses one electron in a reaction with oxygen which yields a free radical and superoxide ($O_2\cdot^-$) as shown in Equation (12). The carbanion may also donate one electron to a suitable electron accepting catalyst (A) as shown in Equation (14). The radical formed by Reactions (12)-(14) next combines with molecular oxygen, forming a peroxy radical. The latter reaction (15) is also one of the chain propagating steps in normal autoxidation. The peroxy radical undergoes reaction with a second carbanion in another chain propagating step, which yields another free radical and a peroxy anion. The latter reaction is represented by Equation (16). Reactions (15) and (16) are thus analogous to Reactions (2) and (3) of the classical autoxidation mechanism. The peroxy anion is the primary product of autoxidation in alkaline media. The credibility of Reaction (13) is questionable, since Sawyer, et al. (27) recently presented evidence showing that superoxide is a very weak oxidizing agent.

OXIDATION BY SPECIES OTHER THAN MOLECULAR OXYGEN

In the presence of a reactive substance such as wood a number of intermediate species, including hydrogen peroxide, hydroperoxides, peroxides and various free radicals, may be formed in significant quantities during the course of autoxidation. All of these compounds may directly or indirectly catalyze fatty acid autoxidation, and in some instances they may react directly with fatty acid molecules.

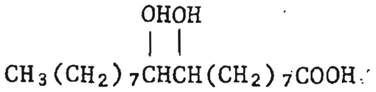
Evolution of hydrogen peroxide during the alkaline autoxidation of carbohydrates was demonstrated by McCloskey, et al. (28). Hydrogen peroxide formation was observed in similar reactions involving lignin model compounds (29), and it also occurred during the autoxidation of methyl linoleate in water (19). Hydrogen peroxide decomposes thermally or catalytically to hydroxyl and hydroperoxy radicals; these in turn may act as autoxidation initiators, or they may interact directly with double bonds. Formation of peroxyacids is a potential reaction of hydrogen peroxide which could be significant at low pH. Peroxyacids readily react with olefins to form epoxides.

The catalysis of autoxidation by free radicals derived from hydrogen peroxides, hydroperoxides and peroxides has been described. In addition, such species may themselves oxidize unsaturated fatty acids without the participation of molecular oxygen. Swift and Dollear (30) allowed methyl oleate hydroperoxide to react with oleic acid under nitrogen at 90°C. The oleic acid was oxidized to 9,10-epoxystearic acid (V) and 9,10-dihydroxystearic acid (VI) by the hydroperoxide. Expoxides and polyperoxides were among the products of



$CH_3(CH_2)_7\overset{O}{CHCH}(CH_2)_7COOH$

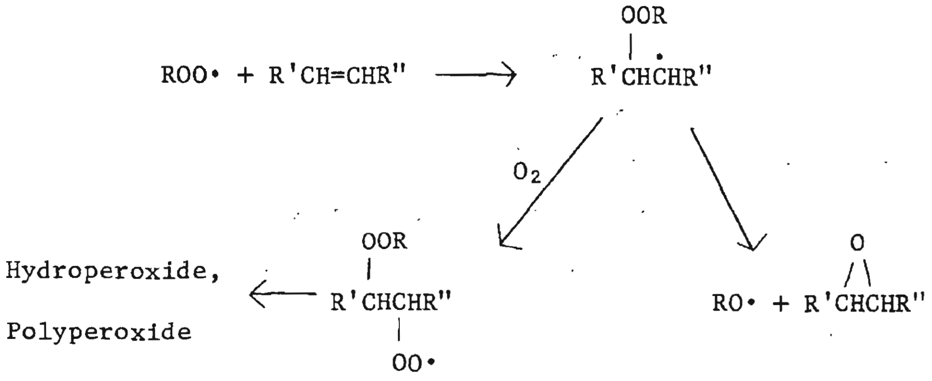
V



$CH_3(CH_2)_7\overset{OH\,OH}{CHCH}(CH_2)_7COOH$

VI

reactions between olefins and peroxy radicals discussed by Brill (31) and Ingold (32), while Sheng and Zajacek (33) obtained high yields of epoxides from reactions between hydroperoxides and olefins in the presence of metal catalysts. The probable mechanism of olefin oxidation by hydroperoxides is shown below (32):



The peroxy radical (ROO•) is formed from the hydroperoxide by Equation (8) or catalytically by Equation (10). Oxidations by hydrogen peroxide and peroxides occur by analogous mechanisms.

OTHER POSSIBLE AUTOXIDATION MECHANISMS

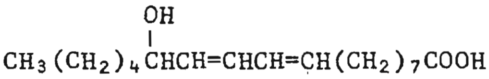
The radical chain mechanism of autoxidation, while almost universally accepted, may not be the only reaction pathway applicable to fatty acid autoxidation. The possibility of a chain-initiating step which involved direct reaction between oxygen and double bonds was discussed by Swern, et al. (10). However, the exact nature of the initial reaction, which would become less significant as the radical chain reaction propagated, was not clarified. Rawls (34) suggested that singlet state oxygen might be indirectly responsible for autoxidation initiation, since that species combined directly with double bonds to form hydroperoxides. Using polarographic techniques, Swern, et al. (35) and Saunders, et al. (36) found evidence which indicated that not all of the peroxidic products of methyl oleate autoxidation were hydroperoxides. Atherton and Hilditch (37) compared autoxidation of methyl oleate at 20 and 120°C. All four of the hydroperoxides (IIa-IId) predicted by the radical chain mechanism were detected at the lower temperature. When the temperature was increased oxidation appeared to occur predominately at the double bond, suggesting a direct interaction between oxygen and the olefin.

SECONDARY AUTOXIDATION PRODUCTS

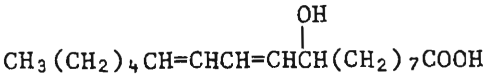
Decomposition of hydroperoxides, which are the primary products of fatty acid autoxidation, results in the formation of numerous secondary products, many of which have been identified. The formation of these products was discussed in the review by Swern, et al. (9). The secondary autoxidation products may be divided into three classes. The first class comprises those compounds which are direct derivatives of the parent fatty acid molecule. These include epoxy, keto and hydroxy acids or esters. Another type of compound is formed by scission of carbon-carbon bonds; unsaturated fatty acids are usually cleaved preferentially at or near the locations of their original double bonds. Cleavage products may be acids, alcohols, carbonyl compounds, peroxides or hydrocarbons. The final class consists of polymeric compounds, the structures of which still have not been ascertained.

EPOXY, KETO AND HYDROXY ACIDS

Inter- or intramolecular decompositions of hydroperoxides without cleavage of carbon-carbon bonds yield hydroxy, epoxy and keto acids or esters. Hydroperoxides decompose thermally to alkoxy radicals; such reactions are catalyzed by transition metal ions as shown in Equation (9). The alkoxy radicals may add hydrogen to form hydroxy compounds. Mixtures of hydroxy acids were found among the autoxidation products of various saturated fatty acids by Franzke, *et al.* (38), while King (39) detected monounsaturated hydroxy esters among the autoxidation products of methyl oleate. Gardner (40) examined secondary products obtained after the ferrous ion catalyzed decomposition of linoleic acid hydroperoxides. Two monohydroxy compounds (VIIa,VIIb) were identified.

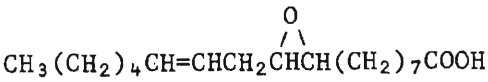

$CH_3(CH_2)_4\overset{\overset{OH}{|}}{C}HCH=CHCH=CH(CH_2)_7COOH$

VIIa

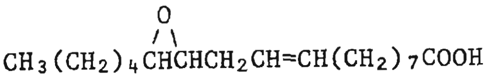

$CH_3(CH_2)_4CH=CHCH=CH\overset{\overset{OH}{|}}{C}H(CH_2)_7COOH$

VIIb

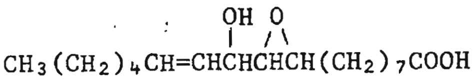
Epoxides, particularly 9,10-epoxystearic acid (V) are commonly detected among the oxidation products of oleic acid and its esters (39,41-43). After autoxidation of linoleic acid, Wu, *et al.* (44) reported the identification of two epoxy acids (VIIIa,VIIIb) and two epoxy-hydroxy acids (IXa,IXb), while Gardner (40) identified the two latter compounds and two epoxy-keto acids (Xa,Xb).


$CH_3(CH_2)_4CH=CHCH_2\overset{\overset{O}{/\ \backslash}}{CHCH}(CH_2)_7COOH$

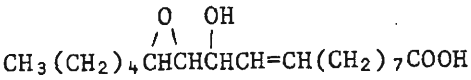
VIIIa


$CH_3(CH_2)_4\overset{\overset{O}{/\ \backslash}}{CHCH}CH_2CH=CH(CH_2)_7COOH$

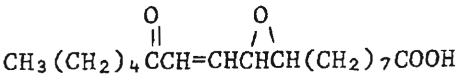
VIIIb


$CH_3(CH_2)_4CH=CH\overset{\overset{OH}{|}}{C}H\overset{\overset{O}{/\ \backslash}}{CHCH}(CH_2)_7COOH$

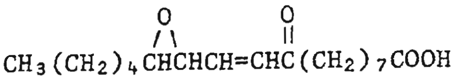
IXa


$CH_3(CH_2)_4\overset{\overset{O}{/\ \backslash}}{CHCH}\overset{\overset{OH}{|}}{C}HCH=CH(CH_2)_7COOH$

IXb


$CH_3(CH_2)_4\overset{\overset{O}{||}}{C}CH=CH\overset{\overset{O}{/\ \backslash}}{CHCH}(CH_2)_7COOH$

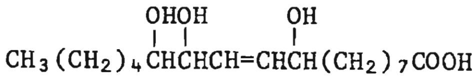
Xa


$CH_3(CH_2)_4\overset{\overset{O}{/\ \backslash}}{CHCH}CH=CH\overset{\overset{O}{||}}{C}(CH_2)_7COOH$

Xb

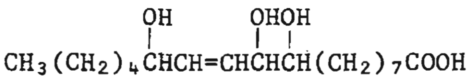
Epoxides formed during reactions between peroxy radicals and unsaturated fatty acids (30) are not true secondary autoxidation products, since they are not derived from compounds formed directly by reaction with molecular oxygen. However, epoxides may also be created by intramolecular decompositions of hydroperoxides, which are primary products of autoxidation (9,43,44).

Another compound often isolated from the secondary autoxidation products of oleic acid is 9,10-dihydroxystearic acid (VI), which results from hydrolysis of 9,10-epoxystearic acid (37,39,42,45-47). Similarly, two *trans* unsaturated trihydroxy octadecenoic acids (**XIa**,**XIb**) were found among the products of autoxidized linoleic acid by Gardner (40) and Terao and Matsushita (48).



$CH_3(CH_2)_4\overset{OH}{C}H\overset{OH}{C}HCH{=}CH\overset{OH}{C}H(CH_2)_7COOH$

XIa

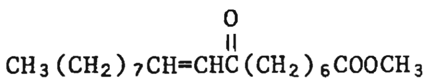


$CH_3(CH_2)_4\overset{OH}{C}HCH{=}CH\overset{OH}{C}H\overset{OH}{C}H(CH_2)_7COOH$

XIb

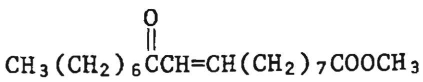
A monounsaturated dihydroxy acid was also tentatively identified after autoxidation of linoleic acid (48).

Ketols and α,β-unsaturated carbonyl compounds are other secondary products of autoxidized fatty acids (9). Individual compounds of those types are seldom isolated, but Ellis (49) and King (39) both reported the identification of two α,β-unsaturated keto esters (**XIIa**,**XIIb**) among the autoxidation products of methyl oleate. Two analogous compounds (**XIIIa**,**XIIIb**) obtained after autoxidation of linoleic acid were identified by Gardner (40).



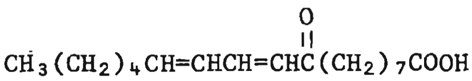
$CH_3(CH_2)_7CH{=}CH\overset{\overset{O}{\parallel}}{C}(CH_2)_6COOCH_3$

XIIa



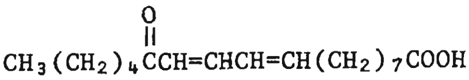
$CH_3(CH_2)_6\overset{\overset{O}{\parallel}}{C}CH{=}CH(CH_2)_7COOCH_3$

XIIb



$CH_3(CH_2)_4CH{=}CHCH{=}CH\overset{\overset{O}{\parallel}}{C}(CH_2)_7COOH$

XIIIa



$CH_3(CH_2)_4\overset{\overset{O}{\parallel}}{C}CH{=}CHCH{=}CH(CH_2)_7COOH$

XIIIb

CLEAVAGE PRODUCTS

Cleavage products which have been identified after autoxidation of fatty acids include saturated straight chain carboxylic acids (XIV), dicarboxylic acids (XV) and a variety of alcohols, aldehydes and ketones.

$CH_3(CH_2)_nCOOH$ XIV

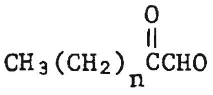
$HOOC(CH_2)_nCOOH$ XV

$OHC(CH_2)_nCOOH$ XVI

$CH_3(CH_2)_nCHO$ XVII

$CH_3(CH_2)_nCH{=}CHCHO$ XVIII

$CH_3(CH_2)_nCH{=}CHCH{=}CHCHO$ XIX



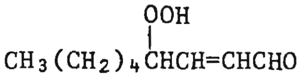
$CH_3(CH_2)_n\overset{\overset{\displaystyle O}{\|}}{C}CHO$

XX

Very complex product mixtures were recovered after autoxidation of saturated fatty acids (38). The predominate cleavage products obtained from autoxidation of oleic acid and its esters (37,39,41,42,45-47,49) were nonanoic acid (XIV, n=7), octanoic acid (XIV, n=6), nonanedioic acid (XV, n=7) and octanedioic acid (XV, n=6). Similarly, hexanoic acid (XIV, n=4) and nonanedioic acid were the major cleavage products of autoxidized linoleic acid identified in one investigation (47), while dicarboxylic acids possessing seven, eight and nine carbon atoms were found after autoxidation of methyl linoleate in water (19).

An aldehyde acid (XVI) was tentatively identified by Ellis (49) after autoxidation of oleic acid, and aldehyde acids were found among the autoxidation products of methyl linoleate by Schoellner and Herzschuh (50). A number of aldehyde acids were detected among the decomposition products of heated cooking oil by Yasuda, *et al.* (51). Various saturated (XVII) and unsaturated (XVIII, XIX) aldehydes were fatty acid hydroperoxide decomposition products identified by Kimoto and Gaddis (52). Swift, *et al.* (53) isolated 2-undecenal (XVIII, n=7), an α,β-unsaturated aldehyde, after heating methyl oleate hydroperoxide. Cobb and Day (54) identified several α-keto aldehydes (XX) possessing up to eight carbon atoms after autoxidation of methyl linoleate.

The identification of several unique cleavage products after autoxidation of methyl linoleate in water was reported by Schauenstein (19). Included were two hydroperoxides, 4-hydroperoxy-2-nonenal (XXI) and the methyl ester of 8-hydroperoxyoctanoic acid (XXII). Analogous hydroxy compounds, 4-hydroxy-2-nonenal

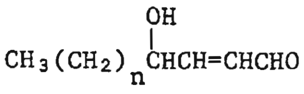


$CH_3(CH_2)_4\overset{OOH}{\overset{|}{C}}HCH{=}CHCHO$

XXI

$HOOCH_2(CH_2)_6COOH$

XXII

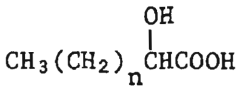


$CH_3(CH_2)_n\overset{OH}{\overset{|}{C}}HCH{=}CHCHO$

XXIII

$HOCH_2(CH_2)_nCOOH$

XXIV



$CH_3(CH_2)_n\overset{OH}{\overset{|}{C}}HCOOH$

XXV

(XXIII, n=4) and the methyl ester of 8-hydroxyoctanoic acid (XXIV, n=6) were also found. Identification of 4-hydroxy-2-octenal (XXIII, n=3) was reported by Esterbauer, et al. (55), who also isolated 2-hydroxyheptanoic acid (XXV, n=4).

The development of combined gas chromatography-mass spectrometry has encouraged numerous investigations into the nature of the secondary autoxidation products obtained from edible fats and oils during deep fat frying. Saturated and unsaturated hydrocarbons, aldehydes, ketones and alcohols were all detected among the volatile oxidation products (56-58). The acidic autoxidation products also comprised very complex mixtures consisting of saturated and unsaturated carboxylic acids, dicarboxylic acids, keto acid, aldehyde acids and hydroxy acids (51,58,59).

POLYMERIC FATTY ACID AUTOXIDATION PRODUCTS

While many of the hydroperoxides and hydroperoxide decomposition products formed during fatty acid autoxidation have been identified, only limited success has been realized in attempts to characterize the polymeric products created during such reactions. Swern, et al. (46) provided evidence which suggested the existence of ether bonds in the polymers, but formation of carbon-carbon bonds and peroxide linkages has also been postulated (9).

RESULTS AND DISCUSSION

The reactions of molecular oxygen with neat fats and oils under mild conditions have been extensively investigated. However, little attention has been paid to the autoxidation of fatty acids or fatty acid derivatives in aqueous systems, and even less interest has been expressed in their reactions with oxygen and alkali. The present investigation focused upon the reactions of fatty acid soaps and fatty acid methyl esters with oxygen in systems containing aqueous alkali. The magnitudes of temperatures and oxygen pressure exceeded those normally associated with autoxidation, but represented conditions which might be encountered during oxygen-alkali delignification of wood or pulp.

Preliminary reactions were carried out to facilitate identification of the oxidation products formed during reactions of the fatty acid derivatives with oxygen and aqueous alkali. The relative reactivities of individual compounds were also compared in the preliminary study. A half factorial experimental design was subsequently developed, in which the effects of selected variables on the degradation of fatty acid esters were more thoroughly investigated. The results of the factorial design were first interpreted from a perspective which considered only potential yields of tall oil fatty acids. Yields of unreacted fatty acid esters and free fatty acids were measured independently in all reactions. The free acids were derived from esters which underwent saponification, but not oxidation, during the course of reaction. Yields of the major acidic oxidation products were also measured for all reactions associated with the half factorial design. The effects of variations in reaction conditions on the distribution of reaction products were discussed, and reaction mechanisms accounting for formation of the observed products were postulated.

OXIDATIONS OF FATTY ACID SOAP SOLUTIONS

During the preliminary stages of the experimental program alkaline solutions of fatty acid soaps were oxidized in a stirred, Teflon-lined reactor. Fatty acids were first dissolved in 0.3N sodium hydroxide. The soap solutions were then heated to 120°C and pressurized with oxygen to 970 kPa (6.9 kPa = 1.0 psi). During one of the reactions a fatty acid mixture containing 910 mg oleic acid and 35 mg linoleic acid underwent oxidation for 8 hr, while a mixture containing 95 mg oleic acid, 1190 mg linoleic acid and 113 mg linolenic acid was oxidized for 12 hr in a second reaction. Fatty acids in the starting materials

$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

Oleic Acid

$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$

Linoleic Acid

$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$

Linolenic Acid

and reaction products were analyzed by gas-liquid chromatography as their methyl esters. The results of the analyses are presented in Table I.

TABLE I

OXIDATIONS OF AQUEOUS ALKALINE SOAP SOLUTIONS[a]

Reaction No.	Time, hr	Weights of Fatty Acids, mg						Percent Yields		
		Oleic		Linoleic		Linolenic				
		Initial	Final	Initial	Final	Initial	Final	Oleic	Linoleic	Linolenic
1	8	910	740	35	2	--	--	81	6	--
2	12	95	80	1190	162	113	0	84	14	0

---

[a] Oxidations conducted in 200 mL 0.3N NaOH at 120°C under 690 kPa O_2 pressure.

The reactivities of the fatty acids increased with increasing degrees of unsaturation, as was expected (8-10). The monounsaturated compound, oleic acid, was oxidized to a lesser extent than linoleic acid, which possessed two double bonds separated by an "activated" methylene group. Linolenic acid (cis,cis,cis-9,12,15-octadecatrienoic acid) was present in the starting material used in Reaction (2). This acid, which contained three methylene interrupted double bonds, was completely consumed.

OXIDATIONS OF FATTY ACID METHYL ESTERS

A series of oxidations was next carried out in which fatty acid methyl esters were the starting materials. Two unsaturated esters, methyl oleate and methyl linoleate, were investigated separately in several reactions, while one oxidation was carried out using a pure saturated ester, methyl palmitate. Two identical mixtures containing four saturated esters were oxidized in another pair of reactions. Those compounds, methyl palmitate, methyl stearate, methyl eicosanoate and methyl docosanoate, were derived from straight chain saturated fatty acids containing from sixteen to twenty-two carbon atoms.

$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$ Methyl Oleate	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOCH_3$ Methyl Linoleate
$CH_3(CH_2)_{14}COOCH_3$ Methyl Palmitate	$CH_3(CH_2)_{16}COOCH_3$ Methyl Stearate
$CH_3(CH_2)_{18}COOCH_3$ Methyl Eicosanoate	$CH_3(CH_2)_{20}COOCH_3$ Methyl Docosanoate

All the methyl esters were oxidized in the presence of a substrate, either cotton linters or preextracted wood meal. Prior to each reaction, the substrate was impregnated with a pure ester or mixture of esters. The impregnated substrate was mixed thoroughly with an aqueous solution of alkali, either sodium hydroxide, sodium carbonate or sodium bicarbonate. The volume of water was adjusted to effect complete absorption of the alkali solution by the substrate. The reactants thus comprised a porous mass of high surface area, allowing intimate contact with the gaseous oxygen. The oxidations were carried out in a 1 liter modified Parr bomb which was not stirred or agitated. The conditions for this series of reactions are listed in Table II, while the yields of unoxidized starting materials are reported in Table III. Fatty acids recovered as unchanged esters are differentiated from those which were saponified and recovered as free acids.

TABLE II

OXIDATIONS OF FATTY ACID METHYL ESTERS: REACTION CONDITIONS

Reaction No.	Substrate	Temp., °C	Time, hr	Pressure O_2, kPa	Alkali
3	50 g Wood meal	140	4	970	11 g NaOH
4	50 g Wood meal	140	4	970	11 g NaOH
5	50 g Wood meal	140	4	970	11 g NaOH
6	50 g Wood meal	140	4	970	14.6 g Na_2CO_3
7	30 g Cotton linters	130	5	2100	11 g NaOH
8	30 g Cotton linters	130	5	2100	23.1 g $NaHCO_3$
9	30 g Cotton linters	130	5	2100	11 g NaOH
10	30 g Cotton linters	130	5	2100	11 g NaOH

As was observed during the oxidations of fatty acid soap solutions, the reactivities of the fatty acid methyl esters increased with the extent of unsaturation. The results from Reactions (3)-(5), which were carried out under identical conditions using three different fatty acid esters, showed that methyl linoleate was oxidized to a greater extent than methyl oleate, while methyl palmitate was by far the most stable compound.

TABLE III

OXIDATIONS OF FATTY ACID METHYL ESTERS: FATTY ACID YIELDS

Reaction No.	Starting Material and Weight of Methyl Ester, g		Unoxidized Starting Material Weights as Methyl Esters, g			Total Yield, %
			Esters	Acids	Total	
3	Methyl palmitate	5.00	N.D.	N.D.	4.47	89
4	Methyl oleate	5.00	N.D.	N.D.	2.46	49
5	Methyl linoleate	5.00	0.07	1.58	1.65	33
6	Methyl linoleate	5.00	1.25	0.16	1.41	28
7	Methyl palmitate	1.11	0	1.04	1.04	94
	Methyl stearate	0.77	0	0.71	0.71	92
	Methyl eicosanoate	0.45	0	0.40	0.40	89
	Methyl docosanoate	0.52	0	0.49	0.49	94
8	Methyl palmitate	1.11	0.98	0.01	0.99	89
	Methyl stearate	0.77	0.70	0.01	0.71	92
	Methyl eicosanoate	0.45	0.40	0	0.40	89
	Methyl docosanoate	0.52	0.46	0	0.46	88
9	Methyl oleate	4.00	0	3.53	3.53	88
10	Methyl linoleate	4.00	0	2.40	2.40	60

Particularly noteworthy among the results presented in Table III is the effect of alkali upon saponification of the fatty acid methyl esters. Equivalent weights of methyl linoleate were oxidized in Reactions (5) and (6), and the reaction conditions differed only in the nature of the alkali. The extents of linoleate degradation were nearly the same in both reactions. However, the unoxidized starting material was almost completely saponified by sodium hydroxide, but it was saponified only to a limited extent when the hydroxide was replaced with carbonate. Similarly, Reactions (7) and (8) were carried out in systems which contained either sodium hydroxide or sodium bicarbonate, but which were otherwise identical. The yields of starting material approached or exceeded 90% after both reactions. Sodium hydroxide effected complete saponification of the esters, while almost no saponification occurred in the system charged with bicarbonate.

While the results of Reactions (1)-(10) provided other insights into the behavior of fatty acids and fatty acid esters during reactions with oxygen and alkali, identification of reaction products was the primary objective of those preliminary oxidations. Product analyses were attempted after each reaction. Although no oxidation products of saturated fatty acids were detected, a large number of compounds were eventually identified after oxidations of the unsaturated fatty acids and esters. The results of the product analyses are discussed in later sections.

DEVELOPMENT OF THE HALF FACTORIAL EXPERIMENTAL DESIGN

After the preliminary reactions had been completed, a half factorial experimental design was developed to investigate the effects of major reaction variables on the degradation of tall oil fatty acid esters by oxygen and alkali. This program was implemented and interpreted according to procedures described by Davies (60).

VARIABLES AND COMPOUNDS INVESTIGATED

The effects of five variables on the reactions of two fatty acid methyl esters, methyl oleate and methyl linoleate, were investigated. The five variables incorporated into the experimental design were defined as temperature, reaction time, oxygen pressure, alkali, and substrate. Each variable was assigned two levels, a high value and a low value, representing the extreme conditions likely to be encountered during oxygen-alkali delignification. The temperatures were 100 and 160°C, the reaction times were 2 and 8 hr, and the oxygen pressures were 690 and 3500 kPa. The high and low levels of alkali were defined as sodium bicarbonate and sodium hydroxide, respectively, based on the assumption that more extensive fatty acid oxidation would occur in a system containing the weaker base. Because an antioxidant effect associated with lignin was expected, cotton linters and wood meal were chosen as the high and low levels, respectively, of the substrate variable.

The absolute quantities of sodium hydroxide, sodium bicarbonate, wood meal and cotton linters employed in all reactions constituting the half factorial design are shown in Table IV. Also enumerated in the table are the high and low magnitudes of the other three variables. In all reactions associated with the half factorial design, each variable was held at one of the two levels shown. To satisfy the complete design, each variable was maintained at its higher level in exactly one-half of all reactions, and at its lower level in the remainder.

TABLE IV

VARIABLES INCORPORATED INTO THE HALF FACTORIAL DESIGN

Variable	Low Level	High Level
Temperature	100°C	160°C
Reaction time	2 hours	8 hours
Oxygen pressure	690 kiloPascals	3500 kiloPascals
Alkali	11 g NaOH	23.1 g $NaHCO_3$
Substrate	50 g wood meal	30 g cotton linters

Temperature

Temperature was included among the variables investigated to determine whether high or low magnitudes might be more conducive to recovery of tall oil fatty acids. Comparison of the influence of temperature with the effects of other variables could aid determination of reaction conditions compatible with both delignification and tall oil fatty acid recovery. The temperature limits chosen represented the probable extremes of any potential oxygen-alkali delignification process. The reaction between oxygen and wood is very slow below

100°C, while high temperatures promote excessive degradation of cellulose. All reactions were initiated at the same temperature, 80°C. The rise to the assigned temperature level was effected using a constant temperature oil bath, and it was further promoted by the exothermic reaction between oxygen and the substrate.

Reaction Time

The effect of reaction time on oxidation of the fatty acid esters was also examined to permit its direct comparison with the effect of other variables. The lower level chosen for this variable was 2 hr. Usually no more than one hour was required for the reaction systems to attain thermal equilibrium.

Oxygen Pressure

The influence of oxygen pressure on the degradation of fatty acids is not as straightforward as the effects of either temperature or reaction time. During normal fatty acid autoxidation, little increase in the rate of reaction is observed when the oxygen pressure is increased beyond a critical magnitude, which depends on the nature of the reactant, and which may have an absolute value as low as 25 kPa (6,7). Oxygen pressure remains a significant variable only if chain propagating free radicals are created at a rate which exceeds the rate of reaction between those short-lived radicals and oxygen. At high pressures reactions of the radicals with oxygen are much more rapid than chain initiating or chain terminating reactions, and no increase in the overall rate of autoxidation is achieved when the pressure is raised further. Oxygen pressure was included among the variables examined in this investigation to determine if a similar situation would exist in the complex, heterogeneous system encountered during delignification. The low level of this variable was far above the expected rate-limiting critical value associated with normal autoxidation and lower than the magnitudes usually employed in oxygen-alkali delignification.

The high level of oxygen pressure was limited by the structural capabilities of the reaction vessel.

Alkali

The high and low levels of alkali were defined as sodium bicarbonate and sodium hydroxide, respectively. Equimolar amounts of each base were employed in all reactions. Bicarbonate was chosen as the higher level of this variable on the basis of previous work by Pearl and Dickey (61), who found that tall oil losses during oxygen-alkali delignification increased if hydroxide was replaced with carbonate or bicarbonate.

Substrate

Pearl and Dickey (61) also observed a "protective effect" related to wood when tall oil fatty acids underwent reaction with oxygen and alkali; the presence of wood in the reaction system retarded degradation of the fatty acids. To further investigate the protective effect of wood on fatty acid oxidation, a fifth variable, defined as substrate, was included in the experimental program. Lignin-free cotton linters were chosen as the higher level of this variable, while preextracted loblolly pinewood meal was defined as its lower level.

Fatty Acid Esters

Methyl oleate, a monounsaturated ester, and methyl linoleate, which possesses two double bonds, were the fatty acid derivatives chosen as starting materials for this investigation. Oleic acid and linoleic acid are by far the two most important tall oil fatty acids (5), both in terms of abundance and value. Saturated fatty acids are also important tall oil components, but the preliminary reactions (Table III) had shown that such compounds were very resistant to reaction with oxygen and alkali. Therefore, to simplify the system, only reactions of the two unsaturated compounds were investigated. Although the fatty acids in wood exist primarily as triglycerides, methyl esters were utilized because of the relative ease with which they could be obtained. The quantities of esters employed, 1.72 g methyl oleate and 2.12 g methyl linoleate, were about eight times the amounts which occur naturally in wood. Because the methyl oleate starting material contained some impurities, 0.16 g of unidentified fatty acids or esters were also present in each reaction.

Reaction System

All of the reactions comprising the final half factorial experimental plan were designed to represent a high consistency oxygen-alkali delignification process. Prior to each reaction, the fatty acid esters were dissolved in acetone and slurried with substrate (50 g wood meal or 30 g cotton linters). The acetone was removed by evaporation under reduced pressure, leaving the substrate impregnated with the fatty acid methyl esters.

To make the system consistent with that employed by Pearl and Dickey (3), the alkali charge in every reaction was 17% (expressed as Na_2O) based on 50 g dry wood. The alkali was dissolved in 180 mL water, and the alkali solutions were completely absorbed by the porous substrates.

FULL FACTORIAL EXPERIMENTAL DESIGN

A full factorial design incorporating all five of the variables listed in Table IV would require thirty-two experiments, and it would include all possible combinations of the five variables at their high and low levels. Each variable would be at its high level in sixteen reactions and at its low level in the other sixteen. Factorial designs allow simultaneous and independent measurements of effects and interactions for several variables in a minimum number of experiments. The overall effect of a variable is defined as its main effect. Interactions exist if the effect of a variable is dependent on the level of one or more of the other variables. An interaction between two single variables is a two-factor interaction. Interactions among three, four or five variables are three-factor, four-factor or five-factor interactions. A full factorial plan for all five variables would allow measurement of five main effects, ten two-factor interactions, ten three-factor interactions, five four-factor interactions and one five-factor interaction. The effects and interactions together would thus represent thirty-one unique pieces of information derived from thirty-two unique trials.

Main Effects of Variables

The main effect of a variable is the average change in a response, measured over all reactions, which results when the magnitude of the variable is raised from its lower level to its higher level. The response is an arbitrarily chosen measurement taken from each reaction. The main effect of a variable is calculated by determining the average response in all those reactions involving the variable at its lower level, and subtracting that quantity from the average response determined in all reactions involving the variable at its higher level.

Interactions Among Variables

Interactions become important if the effect of a variable depends upon the level of one or more of the other variables. To calculate a two-factor interaction between any two variables, the effects of one variable must be considered independently in the two sets of reactions defined by the high and low levels of the other variable. The effect of the first variable is calculated in those reactions which involve the second variable only at its lower level. That quantity is subtracted from the effect of the first variable which is derived from those reactions involving the second variable only at its higher level. The difference between those two effects, which is divided by two to normalize it on the same basis as the main effects, defines the two-factor interaction. If the magnitude of a two-factor interaction is significant, then the main effect of either variable may be meaningless unless consideration is given to the level of the other.

A three-factor interaction exists if the two-factor interaction between any two variables is dependent upon the level of a third variable. Higher order interactions, which involve four or more variables, are defined similarly. By definition, all interactions are symmetrical. The interaction between any two variables will always possess the same sign and magnitude, regardless of how the interaction is calculated. In other words, if the effect of one variable depends upon the level of another, then the inverse is also true. Similarly, an interaction among any group of three or more variables may be considered as the interaction of any one of them with the combined interaction of the others.

FRACTIONAL FACTORIAL DESIGNS

While all effects and interactions may be determined unambiguously in a full factorial design, the magnitudes of higher order interactions are often negligibly small in comparison with the main effects and lower order interactions. Because of this, fractional factorial designs may be devised in which the effects and lower order interactions of certain variables are confounded with the higher order interactions of other variables. Confounding occurs when the experimental plan is purposely designed such that two or more different effects or interactions are represented by the same calculation. When an effect or interaction is confounded with another interaction which is known to be negligible, then the actual quantity determined represents only the nonnegligible entity. By properly confounding interactions and effects, additional variables may be incorporated into an established factorial plan without increasing the number of experiments necessary to satisfy the plan.

THE HALF FACTORIAL EXPERIMENTAL DESIGN

In the present investigation, a full factorial design for four factors, which required sixteen experiments, was first devised. An additional variable was then added to the plan by confounding the main effect of that fifth variable with the four-factor interaction of the original four variables. Each two-factor interaction between the fifth variable and each of the other four variables was similarly confounded with the three-factor interaction of the remaining three.

The experimental design finally developed corresponds to a half factorial design for five variables, which is a specific example of a fractional factorial design. The half factorial design, outlined in Table V, consists of sixteen experiments. If the levels of all variables in all sixteen of those reactions are reversed, another set of sixteen trials, corresponding to the other half of the full factorial design, is obtained. The design shown in Table V may be derived from a full factorial plan involving any four of the variables. The four-factor interaction of the four variables is always confounded with the main effect of the fifth variable in the half factorial design. For example, the main effect of substrate is confounded with the four-factor interaction among temperature, reaction time, oxygen pressure and alkali. The value calculated for the main effect is actually the sum of those two quantities, but the four-factor interaction is presumed to have a numerical value of zero. Similarly, the two-factor interaction between any two variables of the half factorial design is always confounded with the three-factor interaction among the other three. The two-factor interaction between temperature and oxygen pressure, for example, also includes the three-factor interaction among reaction time, alkali and substrate. However, the latter interaction is assumed to be zero.

TABLE V

HALF FACTORIAL DESIGN FOR OXIDATION OF FATTY ACID METHYL ESTERS[a]

Reaction No.	Temperature, °C	Reaction Time, hr	Pressure O_2, kPa	Alkali	Substrate
1F	100	2	690	NaOH	Cotton
2F	160	2	690	NaOH	Wood
3F	100	8	690	NaOH	Wood
4F	160	8	690	NaOH	Cotton
5F	100	2	3500	NaOH	Wood
6F	160	2	3500	NaOH	Cotton
7F	100	8	3500	NaOH	Cotton
8F	160	8	3500	NaOH	Wood
9F	100	2	690	$NaHCO_3$	Wood
10F	160	2	690	$NaHCO_3$	Cotton
11F	100	8	690	$NaHCO_3$	Cotton
12F	160	8	690	$NaHCO_3$	Wood
13F	100	2	3500	$NaHCO_3$	Cotton
14F	160	2	3500	$NaHCO_3$	Wood
15F	100	8	3500	$NaHCO_3$	Wood
16F	160	8	3500	$NaHCO_3$	Cotton
17F[b]	130	5	2100	NaOH	Wood
18F[b]	130	5	2100	NaOH	Wood
19F[b]	130	5	2100	NaOH	Wood
20F[b]	130	5	2100	$NaHCO_3$	Wood
21F[b]	130	5	2100	$NaHCO_3$	Wood

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[a] All reaction systems initially contained 1.72 g methyl oleate and 2.12 g methyl linoleate.

[b] Reactions 17F-21F were not part of the half factorial design, but were included to provide an estimate of experimental error.

On the assumption that all three- and four-factor interactions are negligibly small, the main effects of all five variables, and all ten of their two-factor interactions, may be determined from the sixteen experiments which comprise the half factorial design. However, since there is no replication of experiments, and since all higher-order interactions are already confounded with effects or interactions whose magnitudes may be significant, the design contains no inherent means of determining experimental error. An estimate of variance may be derived by assuming that certain two-factor interactions are negligible. The magnitudes calculated for those interactions are then assumed to represent experimental error only. However, since an external estimate of error was desired, five additional reactions (17F-21F), representing two sets of replicate trials, were also carried out. The temperature, reaction time and oxygen pressure were averages of the high and low values employed in the actual half factorial design. The magnitudes of those three variables were thus 130°C, 5 hr and 2100 kPa, respectively. In one set of trials the alkali was sodium hydroxide, while sodium bicarbonate was used in the other. All five reactions were run in the presence of wood meal. Originally, only two sets of duplicate reactions (17F-18F and 20F-21F) were envisioned, but Reaction 19F was also included because an excessively large discrepancy was observed between the results of Reactions 17F and 18F.

RECOVERY OF FATTY ACID ESTERS, FREE FATTY ACIDS AND OXIDATION PRODUCTS

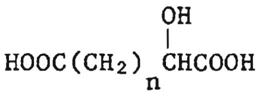
The products of Reactions 1F-21F (Table V) were extracted with ether and fractionated on DEAE Sephadex, a weakly basic anion exchange resin, into three fractions as described by Zinkel and Rowe (62). The first fraction contained unchanged fatty acid methyl esters, neutral compounds which were not retained on the ion exchange resin. The second fraction consisted of weakly acidic material which was eluted from the resin with a saturated solution of carbon dioxide in ether-methanol. Included among the weak acids were free fatty acids formed by saponification of the methyl esters. Since the free fatty acids had not undergone oxidation, they were also considered to be unreacted starting material. The more strongly acidic compounds retained on the ion exchanger after elution with carbon dioxide included many of the fatty acid oxidation products.

The strong acids were stripped from the resin with alternate washings of 1N hydrochloric acid and 1N potassium hydroxide. The fatty acid methyl esters (neutrals), free fatty acids (weak acids) and fatty acid oxidation products (strong acids) were all analyzed by gas-liquid chromatography. The latter were analyzed as their trimethylsilyl derivatives, while the fatty acids were analyzed as their methyl esters. The analytical procedures employed are described in more detail in Appendix III.

To test the efficiency of the overall analytical scheme, a control experiment was carried out in which oxidized wood meal was impregnated with a mixture of fatty acid methyl esters, free fatty acids and selected fatty acid oxidation products. Before impregnation, the wood meal had been oxidized under the same conditions as were employed in Reactions 17F-19F. The impregnated control mixture was analyzed according to the same procedures used during analysis of each of the actual reaction product mixtures. The results of this analysis are presented in Table VI.

The measured recoveries of oleic acid and linoleic acid were 90%. Eighty-nine percent of the methyl oleate was recovered, while all of the methyl linoleate was accounted for. These results suggest that losses of up to 10% may be expected for the free fatty acids and fatty acid methyl esters. The fatty acids and their esters were effectively separated from each other, and from the more strongly acidic oxidation products.

Among the fatty acid oxidation products, good recoveries of the higher dicarboxylic acids (XV) and α-hydroxy acids (XXV) were achieved. One of the latter compounds, 2-hydroxybutyric acid (XXV, n=1), was recovered in excessively high yield. However, this compound has been detected in kraft black liquor (63), and it may be a product of the reaction between wood and oxygen-alkali. Recoveries of the oxidation products tended to decrease as their water solubilities increased. α-Hydroxydicarboxylic acids (XXVI) were fatty acid oxidation products identified during this investigation:



$$HOOC(CH_2)_n\overset{\overset{OH}{|}}{C}HCOOH$$

XXVI

Although two low molecular weight compounds of this class, malic acid (XXVI, n=1) and 2-hydroxypentanedioic acid (XXVI, n=2), were added to the control mixture, they were not detected among the compounds recovered. Both compounds were very soluble in water, and almost insoluble in ether. 2-Hydroxydecanedioic acid (XXVI, n=7) was also added to the control mixture. This compound, appreciably soluble in ether, was recovered in 87% yield.

TABLE VI

TEST OF THE ANALYTICAL PROCEDURE

Compounds Added to Control Mixture Compound - Structure	Wt., mg	Recovery of Compounds Neutrals, mg	%	Weak Acids, mg	%	Strong Acids, mg	%
Methyl oleate	586	523	89				
Methyl linoleate	453	460	102				
Oleic acid	660			593	90		
Linoleic acid	542			487	90		
Nonanoic acid - XIV, n=7	76					27	36
Succinic acid - XV, n=2	187					145	78
Hexanedioic acid - XV, n=4	85					75	88
Heptanedioic acid - XV, n=5	141					145	103
Octanedioic acid - XV, n=6	199					198	99
Nonanedioic acid - XV, n=7	330					345	105
2-Hydroxybutyric acid - XXV, n=1	51					75	147
2-Hydroxypentanoic acid - XXV, n=2	162					175	108
2-Hydroxyhexanoic acid - XXV, n=3	170					168	99
Malic acid - XXVI, n=1	46					0	0
2-Hydroxypentanedioic acid - XXVI, n=2	82					0	0
2-Hydroxydecanedioic acid - XXVI, n=7	149					129	87
9,10-Dihydroxystearic acid - VI	259					70	27

Section 12 List of Attachments

Attachment 1 , section 12: National Organic Standards Board (NOSB), Crops Committee, List 4 Inerts in Pesticide Formulations , Discussion Document, November 2008.

National Organic Standards Board (NOSB)
Crops Committee
List 4 Inerts in Pesticide Formulations
Discussion Document
November 2008

Background:

The National Organic Program (NOP) regulations currently allow the use inert ingredients in pesticide formulations that were previously classified by the EPA
As List 4A- *Minimal Risk Inert Ingredients* and List 4B- *Other ingredients for which EPA has sufficient information to reasonably conclude that the current use pattern in pesticide products will not adversely affect the public health or the environment.*
In accordance with the Food Quality Protection Act, in 2006 the EPA completed reassessments of inert ingredients used in pesticide products to ensure that such products
met human health-based safety standards. Subsequent to that time, the EPA officially notified the NOP that the Inerts List system (Lists 3 and 4) referenced in the NOP regulations in §205.601 and 205.603 is now considered obsolete and no longer in effect.

The NOP needs to amend it's regulations to be in alignment with the modifications the EPA has made to it's regulations. In the meantime, the EPA has agreed to allow the NOP to continue the List 4 designation of allowed materials (as referenced in the August 2004 EPA List 4) while the NOP determines the best way to amend the regulations. The EPA reassessments have removed some materials from their list of minimal risk ingredients (List 4B), which are now prohibited under the NOP. The potential exists for the EPA to add new materials to their list of minimal risk ingredients as well. The EPA minimal risk ingredients can be found in 40 CFR 180.950 – *Tolerance exemptions for minimal risk active and inert ingredients* (attached at the end of this document). As the originator and maintainer of the National List of Allowed and Prohibited Substances in organic production and handling, the NOSB needs to work in concert with the NOP and EPA to accomplish the task of amending NOP inert ingredient regulations as they pertain to the National List.

Current Regulatory Language

§205.601....
m) As synthetic inert ingredients as classified by the Environmental Protection Agency (EPA), for use with nonsynthetic substances or synthetic substances listed in this section and used as an active pesticide ingredient in accordance with any limitations on the use of such substances.
(1) EPA List 4—Inerts of Minimal Concern.
(2) EPA List 3—Inerts of Unknown Toxicity allowed:
(i) Glycerine Oleate (Glycerol monooleate) (CAS #s 37220–82–9)—for use only until December 31, 2006.
(ii) Inerts used in passive pheromone dispensers.
(n) Seed preparations. Hydrogen chloride (CAS # 7647–01–0)—for delinting cotton seed for planting.

§205.603....
(e) As synthetic inert ingredients as classified by the Environmental Protection Agency (EPA), for use with nonsynthetic substances or synthetic substances listed in this section and used as an active pesticide ingredient in accordance with any limitations on the use of such substances.
(1) EPA List 4—Inerts of Minimal Concern.

Plan of Action:

The NOSB will begin public discussion of these matters at their November 2008 meeting.
Public comment is invited to comment on the possible solutions described below.
Public comment is heavily encouraged to identify the number and nature of synthetic materials deemed to be vital in pesticide formulations used in organic farming.

Possible solution options:

1)The NOP has suggested that a substitution of the language in the rule currently as List 4 with the new regulatory reference for 40 CFR 180.950 the minimal risk ingredients (significant correlation to List 4A).

2)Adopt the original 2004 List 4A inerts (Attachment 1) as an itemized list, with ongoing re-assessment through the sunset process.

3) Adopt the minimal risk ingredients currently in 40 CFR 180.950 (significant correlation to List 4A). This would entail a one time adoption of materials currently on this list with ongoing re-assessment through the sunset process.

4) Eliminate blanket inerts lists and adopt a policy of requiring inerts in pesticides to be petitioned individually.

5) Inerts (List 3) currently used in passive pheromone dispensers would be petitioned individually and be subject to regular sunset re-evaluations.

Upon taking the subject under advisement, a final NOSB recommendation could potentially be presented at the Spring 2009 meeting. Considering that the NOSB recommendation will need to be vetted through the EPA, a posting for public comment and NOSB adoption might be more realistically accomplished at the Fall 2009 meeting. Simultaneous to the NOSB review, an Advanced Notice of Proposed Rulemaking (ANPR) would be an important step prior to whichever meeting timetable is selected. Following the vote by the NOSB on a final recommendation on inert ingredients to be included on the National List, proposed rulemaking should proceed.

§ 180.950 Tolerance exemptions for minimal risk active and inert ingredients.

Unless specifically excluded, residues resulting from the use of the following substances as either an inert or an active ingredient in a pesticide chemical formulation, including antimicrobial pesticide chemicals, are exempted from the requirement of a tolerance under FFDCA section 408, if such use is in accordance with good agricultural or manufacturing practices.

(a) *Commonly consumed food commodities.* Commonly consumed food commodities means foods that are commonly consumed for their nutrient properties. The term commonly consumed food commodities shall only apply to food commodities (whether a raw agricultural commodity or a processed commodity) in the form the commodity is sold or distributed to the public for consumption.

(1) Included within the term commonly consumed food commodities are:

(i) Sugars such as sucrose, lactose, dextrose and fructose, and invert sugar and syrup.

(ii) Spices such as cinnamon, cloves, and red pepper

(iii) Herbs such as basil, anise, or fenugreek.

(2) Excluded from the term commonly consumed food commodities are:

(i) Any food commodity that is adulterated under 21 U.S.C. 342.

(ii) Both the raw and processed forms of peanuts, tree nuts, milk, soybeans, eggs, fish, crustacea, and wheat.

(iii) Alcoholic beverages.

(iv) Dietary supplements.

(b) *Animal feed items.* Animal feed items means meat meal and all items derived from field crops that are fed to livestock excluding both the raw and processed forms of peanuts, tree nuts, milk, soybeans, eggs, fish, crustacea, and wheat. Meat meal is an animal feed composed of dried animal fat and protein that has been sterilized. Other than meat meal, the term animal feed item does not extend to any item designed to be fed to animals that contains, to any extent, components of animals. Included within the term animal feed items are:

(1) The hulls and shells of the commodities specified in paragraph (a)(2)(ii) of this section, and cocoa bean.

(2) Bird feed such as canary seed.

(3) Any feed component of a medicated feed meeting the definition of an animal feed item.

(c) *Edible fats and oils.* Edible fats and oils means all edible (food or feed) fats and oils, derived from either plants or animals, whether or not commonly consumed, including products derived from hydrogenating (food or feed) oils, or liquefying (food or feed) fats.

(1) Included within the term edible fats and oils are oils (such as soybean oil) that are derived from the commodities specified in paragraph (a)(2)(ii) of this section when such oils are highly refined via a solvent extraction procedure.

(2) Excluded from the term edible fats and oils are plant oils used in the pesticide chemical formulation specifically to impart their characteristic fragrance and/or flavoring.

(d) [Reserved]

(e) *Specific chemical substances.* Residues resulting from the use of the following substances as either an inert or an active ingredient in a pesticide chemical formulation, including antimicrobial pesticide chemicals, are exempted from the requirement of a tolerance under FFDCA section 408, if such use is in accordance with good agricultural or manufacturing practices.

Chemical	***CAS No.***
Acetic acid, sodium salt	*127–09–3*
Alpha-cyclodextrin	10016–20–3
Amylopectin, acid-hydrolyzed, 1-octenylbutanedioate	113894–85–2
Amylopectin, hydrogen 1-octadecenylbutanedioate	125109–81–1
Animal glue	None
Ascorbic acid (vitamin C)	50–81–7
Beeswax	8012–89–3
Benzoic acid, sodium salt	532–32–1
Beta-cyclodextrin	7585–39–9
Carbonic acid, monopotassium salt	298–14–6
Carbonic acid, monosodium salt (sodium bicarbonate)	144–55–8
Carnauba wax	8015–86–9
Carob gum (locust bean gum)	9000–40–2
Castor oil	8001–79–4
Castor oil, hydrogenated	8001–78–3
Cellulose	9004–34–6
Cellulose acetate	9004–35–7

Cellulose, carboxy methyl ether, sodium salt	9004–32–4
Cellulose, 2-hydroxyethyl ether	9004–62–0
Cellulose, 2-hydroxypropyl ether	9004–64–2
Cellulose, 2-hydroxypropyl methyl ether	9004–65–3
Cellulose, methyl ether	9004–67–5
Cellulose, mixture with cellulose carboxymethyl ether, sodium salt	51395–75–6
Cellulose, pulp	65996–61–4
Cellulose, regenerated	68442–85–3
Citric acid	77–92–9
Citric acid, 2-(acetyloxy)-, tributyl ester	77–90–7
Citric acid, calcium salt	7693–13–2
Citric acid, calcium salt (2:3)	813–94–5
Citric acid, dipotassium salt	3609–96–9
Citric acid, disodium salt	144–33–2
Citric acid, monohydrate	5949–29–1
Citric acid, monopotassium salt	866–83–1
Citric acid, monosodium salt	18996–35–5
Citric acid, potassium salt	7778–49–6
Citric acid, triethyl ester	77–93–0
Citric acid, tripotassium salt	866–84–2
Citric acid, tripotassium salt, monohydrate	6100–05–6
Citric acid, sodium salt	994–36–5
Citric acid, trisodium salt	68–04–2
Citric acid, trisodium salt, dihydrate	6132–04–3
Citric acid, trisodium salt, pentahydrate	6858–44–2
Coffee grounds	68916–18–7
Dextrins	9004–53–9
1,3-Dioxolan-2-one, 4-methyl-(propylene carbonate)	108–32–7
Fumaric acid	110–17–8
Gamma-cyclodextrin	17465–86–0

Gellan gum	71010–52–1
D-Glucitol (sorbitol)	50–70–4
Glycerol (glycerin) (1,2,3-propanetriol)	56–81–5
Guar gum	9000–30–0
Humic acid	1413–93–6
Humic acid, potassium salt	68514–28–3
Humic acid, sodium salt	68131–04–4
Lactic acid, n-butyl ester	138–22–7
Lactic acid, n-butyl ester, (S)	34451–19–9
Lactic acid, ethyl ester	97–64–3
Lactic acid, ethyl ester,(S)	687–47–8
Lanolin	8006–54–0
Lecithins	8002–43–5
Lecithins, soya	8030–76–0
Licorice Extract	68916–91–6
Maltodextrin	9050–36–6
Paper	None
Potassium chloride	7447–40–7
2-Propanol (isopropyl alcohol)	67–63–0
Red cabbage color, expressed from edible red cabbage heads via a pressing process using only acidified water	None
Silica, amorphous, fumed (crystalline free)	112945–52–5
Silica, amorphous, precipitated and gel	7699–41–4
Silica gel	63231–67–4
Silica gel, precipitated, crystalline-free	112926–00–8
Silica, hydrate	10279–57–9
Silica, vitreous	60676–86–0
Soap (The water soluble sodium or potassium salts of fatty acids produced by either the saponification of fats and oils, or the neutralization of fatty acid)	None
Sorbic acid, potassium salt	24634–61–5
Soapbark (Quillaja saponin)	1393–03–9

Sodium alginate	9005–38–3
Sodium chloride	7647–14–5
Syrups, hydrolyzed starch, hydrogenated	68425--17–2
Ultramarine blue (C.I. Pigment Blue 29)	57455--37–5
Urea	57–13–6
Vanillin	121–33–5
Xanthan gum	11138--66–2

Attachment 13, section 9, Chemistry of
Fatty Acid.
(for tall oil see page 31)

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Chemistry of Fatty Acids

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1. INTRODUCTION

Fatty acids, esterified to glycerol, are the main constituents of oils and fats. The industrial exploitation of oils and fats, both for food and oleochemical products, is based on chemical modification of both the carboxyl and unsaturated groups present in fatty acids. Although the most reactive sites in fatty acids are the carboxyl group and double bonds, methylenes adjacent to them are activated, increasing their reactivity. Only rarely do saturated chains show reactivity. Carboxyl groups and unsaturated centers usually react independently, but when in close proximity, both may react through neighboring group participation. In enzymatic reactions, the reactivity of the carboxyl group can be influenced by the presence of a nearby double bond.

The industrial chemistry of oils and fats is a mature technology, with decades of experience and refinement behind current practices. It is not, however, static. Environmental pressures demand cleaner processes, and there is a market for new products. Current developments are in three areas: "green" chemistry, using cleaner processes, less energy, and renewable resources; enzyme catalyzed reactions, used both as environmentally friendly processes and to produce tailor-made products; and novel chemistry to functionalize the carbon chain, leading to new

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Bailey's Industrial Oil and Fat Products, Sixth Edition, Six Volume Set.
Edited by Fereidoon Shahidi.

compounds. Changing perceptions of what is nutritionally desirable in fat-based products also drives changing technology; interesterification is more widely used and may replace partial hydrogenation in the formulation of some modified fats.

The coverage in this chapter is necessarily selective, focusing on aspects of fatty acid and lipid chemistry relevant to the analysis and industrial exploitation of oils and fats. The emphasis is on fatty acids and acylglycerols found in commodity oils and the reactions used in the food and oleochemical industries. The practical application of this chemistry is dealt with in detail in other chapters. Current areas of research, either to improve existing processes or to develop new ones, are also covered, a common theme being the use of chemical and enzyme catalysts. Compounds of second-row transition metals rhodium and ruthenium and the oxides of rhenium and tungsten have attracted particular interest as catalysts for diverse reactions at double bonds. Recent interest in developing novel compounds by functionalizing the fatty acid chain is also mentioned. To date, few of these developments have found industrial use, but they suggest where future developments are likely. A number of recent reviews and books cover and expand on topics discussed here (1–10).

2. COMPOSITION AND STRUCTURE

2.1. Fatty Acids

Fatty acids are almost entirely straight chain aliphatic carboxylic acids. The broadest definition includes all chain lengths, but most natural fatty acids are C_4 to C_{22}, with C_{18} most common. Naturally occurring fatty acids share a common biosynthesis. The chain is built from two carbon units, and *cis* double bonds are inserted by desaturase enzymes at specific positions relative to the carboxyl group. This results in even-chain-length fatty acids with a characteristic pattern of methylene interrupted *cis* double bonds. A large number of fatty acids varying in chain length and unsaturation result from this pathway.

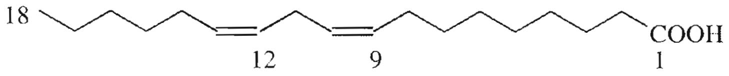
Systematic names for fatty acids are too cumbersome for general use, and shorter alternatives are widely used. Two numbers separated by a colon give, respectively, the chain length and number of double bonds: octadecenoic acid with 18 carbons and 1 double bond is therefore 18:1. The position of double bonds is indicated in a number of ways: explicitly, defining the position and configuration; or locating double bonds relative to the methyl or carboxyl ends of the chain. Double-bond position relative to the methyl end is shown as n-x or ωx, where x is the number of carbons from the methyl end. The n-system is now preferred, but both are widely used. The position of the first double bond from the carboxyl end is designated Δx. Common names (Table 1) may be historical, often conveying no structural information, or abbreviations of systematic names. Alternative repre-

TABLE 1. Fatty Acids in Commodity Oils and Fats. (a) Nomenclature and Structure.

Fatty acid	Common name	Formula	Chain length
4:0	butyric	$CH_3(CH_2)_2CO_2H$	short
6:0	caproic	$CH_3(CH_2)_4CO_2H$	short
8:0	caprylic	$CH_3(CH_2)_6CO_2H$	short/medium
10:0	capric	$CH_3(CH_2)_8CO_2H$	medium
12:0	lauric	$CH_3(CH_2)_{10}CO_2H$	medium
14:0	myristic	$CH_3(CH_2)_{12}CO_2H$	medium
16:0	palmitic	$CH_3(CH_2)_{14}CO_2H$	
18:0	stearic	$CH_3(CH_2)_{16}CO_2H$	
18:1 9*c*	oleic	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$	
18:2 9*c*12*c*	linoleic	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6CO_2H$	
18:3 9*c*12*c*15*c*	α-linolenic	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6CO_2H$	
22:1 13*c*	erucic	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}CO_2H$	long
20:5 5*c* 8*c*11*c*14*c*17*c*	EPA*	$CH_3CH_2(CH{=}CHCH_2)_5(CH_2)_2CO_2H$	long
22:6 4*c*7*c*10*c*13*c*16*c*19*c*	DHA*	$CH_3CH_2(CH{=}CHCH_2)_6CH_2CO_2H$	long

*Abbreviations of the systematic names eicosapentaenoic acid and docosahexaenoic acid.

sentations of linoleic acid (**1**) are 9*Z*,12*Z*-octadecadienoic acid; 18:2 9c12c; 18:2 n-6; 18:2 ω6; 18:2 Δ9,12; or $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$.



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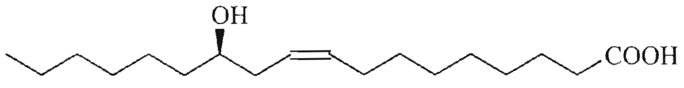
The terms *cis* and *trans*, abbreviated *c* and *t*, are used widely for double-bond geometry; as with only two substituents, there is no ambiguity that requires the systematic *Z*/*E* convention. An expansive discussion of fatty acid and lipid nomenclature and structure appears in Akoh and Min (1).

TABLE 1. (b) Occurrence.

Fatty Acid	Significant Sources
4:0	butter, dairy fats
6:0	(coconut, palm kernel)
8:0	(coconut, palm kernel)
10:0	(coconut, palm kernel)
12:0	coconut, palm kernel
14:0	coconut, palm kernel
16:0	cottonseed, palm
18:0	cocoa butter, tallow
18:1 9c	cottonseed, olive, palm, rape
18:2 9c12c	corn, sesame, soybean, sunflower
18:3 9c12c15c	linseed
20:1 13c	high erucic rape
20:5 5c8c11c14c17c	fish and animal fats
22:6 4c7c10c13c16c19c	fish and animal fats

Over 1000 fatty acids are known, but 20 or less are encountered in significant amounts in the oils and fats of commercial importance (Table 1). The most common acids are C_{16} and C_{18}. Below this range, they are characterized as short or medium chain and above it as long-chain acids.

Fatty acids with *trans* or non-methylene-interrupted unsaturation occur naturally or are formed during processing; for example, vaccenic acid (18:1 11*t*) and the conjugated linoleic acid (CLA) rumenic acid (18:2 9*t*11*c*) are found in dairy fats. Hydroxy, epoxy, cyclopropane, cyclopropene acetylenic, and methyl branched fatty acids are known, but only ricinoleic acid (12(*R*)-hydroxy-9*Z*-octadecenoic acid) (**2**) from castor oil is used for oleochemical production. Oils containing vernolic acid (12(*S*),13(*R*)-epoxy-9*Z*-octadecenoic acid) (**3**) have potential for industrial use.



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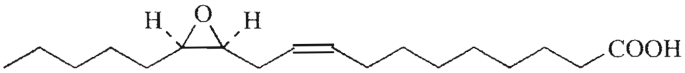

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Typical fatty acid composition of the most widely traded commodity oils is shown in Table 2.

TABLE 2. Fatty Acid Content of the Major Commodity Oils (wt%).

	16:0 (wt%)	18:1 (wt%)	18:2 (wt%)	18:3 (wt%)	Other [Fatty Acid (wt%)]
butter	28	14	1	1	4:0 (9); 6:0–12:0 (18); 14:0 (14) + odd chain and *trans*
castor	1	3	4		18:1(OH) (90)
coconut	9	6	2		8:0 (8); 10:0 (7); 12:0 (48); 14:0 (18)
corn	13	31	52	1	
cottonseed	24	19	53		
fish*	14	22	1		16:1 n-7 (12); 20:1 n-9 (12); 22:1 n-11 (11); 20:5 n-3 (7); 22:6 n-3 (7)
groundnut (peanut)	13	37	41		C_{20}–C_{24} (7)
lard	27	44	11	1	14:0 (2) 18:0 (11) + long and odd chain
linseed	6	17	14	60	
olive	10	78	7		
palm	44	40	10		
palm kernel	9	15	2		8:0 (3); 10:0 (4); 12:0 (49); 14:0 (16)
rape**	4	56	26	10	
sesame	9	38	45		18:0 (6)
soybean	11	22	53	8	
sunflower	6	18	69		18:0 (6)
tallow	26	31	2		14:0 (6) 18:0 (31) + long and odd chain

Typical midrange values shown; the balance are minor components. Data from (9).

*Cod liver oil.

**Low-erucic-acid rape, e.g., Canola.

Most commodity oils contain fatty acids with chain lengths between C_{16} and C_{22}, with C_{18} fatty acids dominating in most plant oils. Palm kernel and coconut, sources of medium-chain fatty acids, are referred to as lauric oils. Animal fats have a wider range of chain length, and high erucic varieties of rape are rich in this C_{22} monoene acid. Potential new oil crops with unusual unsaturation or additional functionality are under development. Compilations of the fatty acid composition of oils and fats (6, 9, 11, 12) and less-common fatty acids (13) are available.

The basic structure, a hydrophobic hydrocarbon chain with a hydrophilic polar group at one end, endows fatty acids and their derivatives with distinctive properties, reflected in both their food and industrial use. Saturated fatty acids have a straight hydrocarbon chain. A *trans*-double bond is accommodated with little change in shape, but a *cis* bond introduces a pronounced bend in the chain (Fig. 1).

In the solid phase, fatty acids and related compounds pack with the hydrocarbon chains aligned and, usually, the polar groups together. The details of the packing, such as the unit cell angles and head-to-tail or head-to-head arrangement depend on the fatty acid structure (Fig. 2).

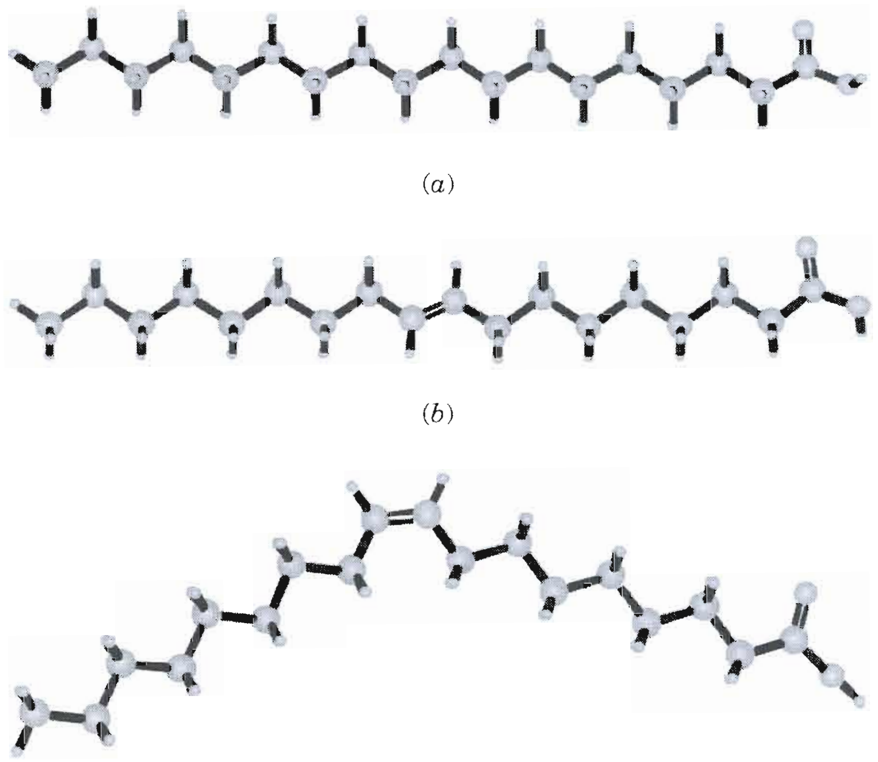
The melting point increases with chain length and decreases with increased unsaturation (Table 3). Among saturated acids, odd chain acids are lower melting than adjacent even chain acids. The presence of *cis*-double bonds markedly lowers the melting point, the bent chains packing less well. *Trans*-acids have melting points much closer to those of the corresponding saturates. Polymorphism results in two or more solid phases with different melting points. Methyl esters are lower melting than fatty acids but follow similar trends.

Fatty acid salts and many polar derivatives of fatty acids are amphiphilic, possessing both hydrophobic and hydrophilic areas within the one molecule. These are surface-active compounds that form monolayers at water/air and water/surface interfaces and micelles in solution. Their surface-active properties are highly dependent on the nature of the polar head group and, to a lesser extent, on the length of the alkyl chain. Most oleochemical processes are modifications of the carboxyl group to produce specific surfactants.

TABLE 3. Melting Points of Some Fatty Acids and Methyl Esters Illustrating the Effect of Chain Length and Unsaturation.

Fatty acid	Melting Point (°C)	Fatty Acid	Melting Point (°C)
16:0	62.9 (30.7)		
17:0	61.3 (29.7)		
18:0	70.1 (37.8)		
18:1 9*c*	16.3, 13.4	18:1 9*t*	45
18:2 9*c*12*c*	−5	18:2 9*t*12*t*	29
19:0	69.4 (38.5)		
20:0	76.1 (46.4)		

Values for methyl esters in parenthesis.
Data from (8) and (9).



(*a*)

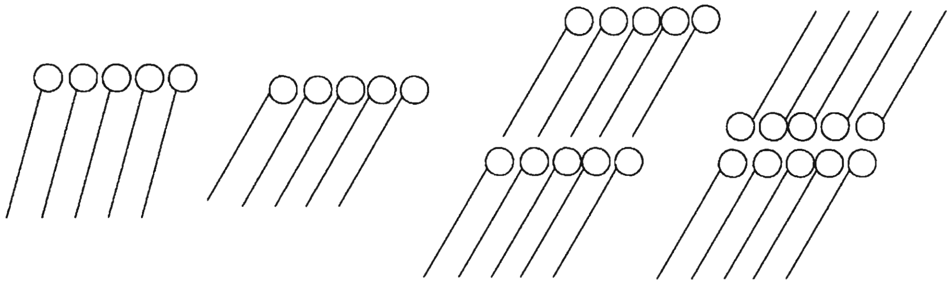
(*b*)

(*c*)

Figure 1. *"Ball and stick" models of (a) stearic acid, 18:0; (b) elaidic acid, 18:1 9t; and (c) oleic acid 18:1 9c. All three lie flat in the plane of the paper. The cis double bond causes a distinct kink in the alkyl chain of oleic acid.*

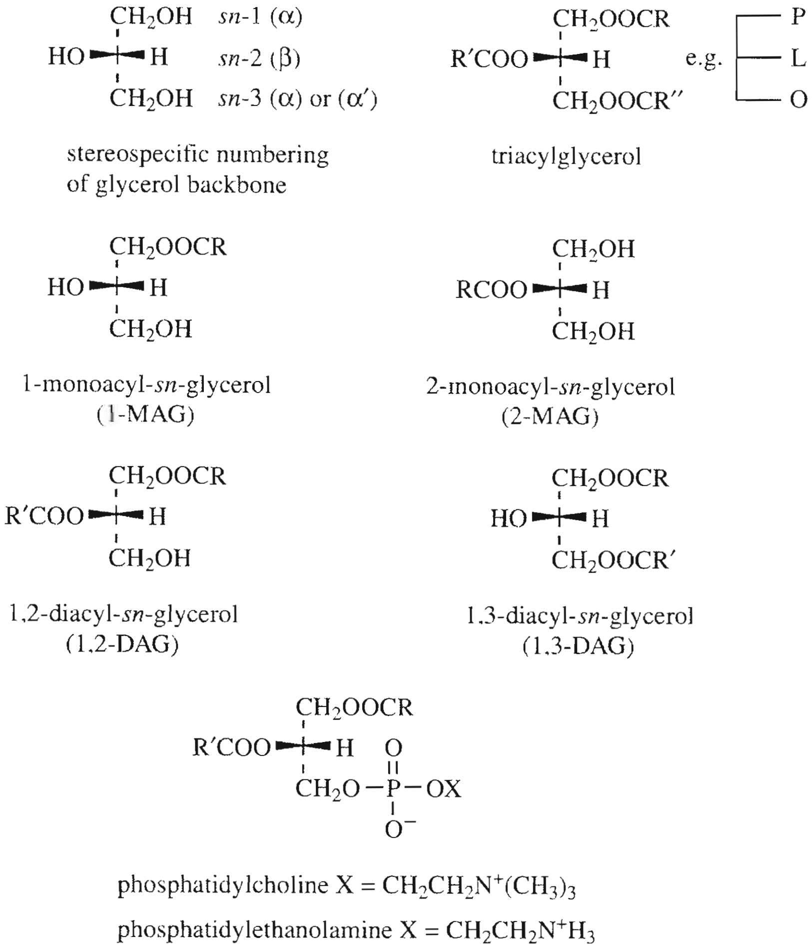
2.2. Acylglycerols

Fatty acids in oils and fats are found esterified to glycerol. Glycerol (1,2,3-trihydroxypropane) is a prochiral molecule. It has a plane of symmetry, but if the primary hydroxyls are esterified to different groups, the resulting molecule is chiral and exists as two enantiomers. The stereospecific numbering system is used to



(*a*) (*b*) (*c*) (*d*)

Figure 2. *Simplified diagram shows packing patterns of fatty acids in the solid phase. (a) and (b): Hydrocarbon tails (straight lines) aligned at different angles to the line of the polar head groups (circles). (c): Head to tail packing. (d): Head to head packing.*



stereospecific numbering of glycerol backbone

triacylglycerol

1-monoacyl-*sn*-glycerol (1-MAG)

2-monoacyl-*sn*-glycerol (2-MAG)

1,2-diacyl-*sn*-glycerol (1,2-DAG)

1,3-diacyl-*sn*-glycerol (1,3-DAG)

phosphatidylcholine $X = CH_2CH_2N^+(CH_3)_3$

phosphatidylethanolamine $X = CH_2CH_2N^+H_3$

Figure 3. *Structure and stereospecific numbering of acylglycerols.*

distinguish between enantiomers. The Fischer projection of glycerol is drawn with the backbone bonds going into the paper and the hydroxyl on the middle carbon to the left. The carbons are then numbered 1 to 3 from the top (Figure 3). The prefix *sn*- (for stereospecific numbering) denotes a particular enantiomer, *rac*- an equal mixture of enantiomers, and *x*- an unknown stereochemistry. In an asymmetric environment such as an enzyme binding site, the *sn*-1 and *sn*-3 groups are not interchangeable and reaction will only occur at one position. Simplified structures are often used; e.g., 1-palmitoyl-2-linoleoyl-3-oleoyl-*sn*-glycerol is abbreviated to PLO or drawn as shown in Figure 3.

Storage fats (seed oils and animal adipose tissue) consist chiefly (~98%) of triacylglycerols, with the fatty acids distributed among different molecular species. With only two fatty acids, a total of eight triacylglycerol isomers are possible, including enantiomers (Table 4). A full analysis of triacylglycerol molecular species is a major undertaking, and for some oils, there are still technical difficulties to be resolved. More commonly, triacylglycerols are distinguished by carbon number (the sum of the fatty acid chain lengths) or unsaturation, using GC or HPLC for analysis. The number of isomers increases as the cube of the number of fatty acids;

TABLE 4. Molecular Species of Triacylglycerols Containing only Palmitic and Oleic Acid.

	PPP	POP	PPO	OPP	POO	OOP	OPO	OOO
enantiomers			*	*	**	**		
carbon number	48	50	50	50	52	52	52	54
double bonds	0	1	1	1	2	2	2	3

Different methods of analysis will give different and often incomplete information about such a mixture. GC analysis will separate molecular species by carbon number (sum of fatty acid chain lengths). Silver-ion HPLC will separate by number of double bonds. Stereospecific analysis measures the proportions of fatty acids at the *sn*-1, *sn*-2, and *sn*-3 positions, but it does not detect individual molecular species.

hence, even in oils with a simple fatty acid composition, many molecular species of triacylglycerol may be present.

Most natural triacylglycerols do not have a random distribution of fatty acids on the glycerol backbone. In plant oils, unsaturated acids predominate at the *sn*-2 position, with more saturated acids at *sn*-1 and *sn*-3. The distribution of fatty acids at the *sn*-1 and *sn*-3 positions is often similar, although not identical. However, a random distribution between these two positions is often assumed as full stereospecific analysis is a time-consuming specialist procedure. In animal fats, the type of fatty acid predominating at the *sn*-2 position is more variable; for example, palmitate may be selectively incorporated as well as unsaturated acids (Table 5).

Only oils that are rich in one fatty acid contain much monoacid triacylglycerol, for example, olive (Table 5), sunflower, and linseed oils containing OOO, LLL, and LnLnLn, respectively. Compilations of the triacylglycerol composition of commodity and other oils are available (8, 9).

The melting behavior of triacylglycerols generally reflects that expected from the fatty acid composition; triacylglycerols rich in long-chain and saturated acids

TABLE 5. Contrasting Triacylglycerol Composition of Some Commodity Oils [Molecular Species (wt%)].

Cocoa butter	Coconut	Lard	Olive	Soybean
POP (18-23)	12,12,8 (12)	PPSt (2)	OOL (11)	LnLL (7)
POSt (36-41)	12,12,10 (6)	StPSt (2)	OOO (43)	LnLO (5)
StOSt (23-31)	12,12,12 (11)	PPO (8)	POP (3)	LLL (15)
	12,12,14 (11)	StOP (13)	POL (4)	LLO (16)
unsymmetrical	14,12,8 (9)	POO (5)	POO (22)	LLS (13)
e.g., SSO <1%		StOO (6)	StOO (5)	LOO (8)
		OPO (18)		LOS (12)
		StPL (2)		OOS (5)
		OOO (12)		
		OPL (7)		

L—linoleic; Ln—linolenic; O—oleic; P—palmitic; S—saturate; St—stearic; 8—8:0; 10—10:0; 12—12:0 (lauric); 14—14:0.

Analysis by methods that do not distinguish all isomers; only major components are listed.

Data from (6).

are high melting, and those rich in polyunsaturated acids are lower melting. However, the situation is complicated by the possibility that the fatty acids can be distributed in different molecular species with different melting points. Oils with similar fatty acid composition may have different solid fat content, polymorphic forms, and melting behavior as a result of a different triacylglycerol composition.

Mono- and diacylglycerols (Figure 3) are not significant components of good quality oils, but elevated levels may be found in badly stored seeds, resulting from the activity of lipolytic enzymes. These compounds are produced industrially by partial hydrolysis or glycerolysis of triacylglycerols for use as food grade emulsifiers. Mono- and diacylglycerols readily isomerize under acid or base catalysis and are normally produced as an equilibrium mixture in which 1(3)-monoacylglycerols or 1,3-diacylglycerols predominate.

Phospholipids (Figure 3) are constituents of membranes and are only minor components of oils and fats, sometimes responsible for cloudiness. They are usually removed during degumming, the residue from soybean oil processing being a source of phospholipids used as food emulsifiers. The term "lecithin" is used very loosely for such material, and it may variously mean phosphatidylcholine, mixed glycerophospholipids, or crude phospholipid extracts from various sources. Where possible, more specific nomenclature or the source and purity should be used (14).

2.3. Bulk Properties

Saponification value and iodine value. Oils and fats are now characterized mainly by their fatty acid composition determined by gas chromatography, replacing the titrimetric and gravimetric assays used previously. However, the saponification value (SV) or equivalent (SE) and iodine value (IV) are still used in specifications and to monitor processes. SE, expressed as grams of fat saponified by one mole of potassium hydroxide, is an indication of the average molecular weight and hence chain length, whereas the IV, expressed as the weight percent of iodine consumed by the fat in a reaction with iodine monochloride, is an index of unsaturation (Table 6). Standard analytical methods are available (15), but these parameters are now often calculated from the fatty acid composition, assuming that the sample is all triacylglycerol (15). Indirect measurement of IV (16, 17) and SV (17) (as well as peroxide and *trans*-content) using FT-NIR spectroscopy have been developed for real-time process monitoring.

Unsaponifiable matter. Oils and fats contain variable amounts of sterols, hydrocarbons, tocopherols, carotenoids, and other compounds, collectively referred to as unsaponifiable matter because they do not produce soaps upon hydrolysis (Table 6). The sterol and tocopherol composition of commodity oils is discussed in another chapter. Some of these minor components are removed during refining, and the resulting concentrates may be useful byproducts, for example, tocopherol antioxidants. Characteristic fingerprints of minor components, particularly phytosterols and tocopherols, are also used to authenticate oils and detect adulteration (18).

TABLE 6. Saponification Equivalent (SE), Saponification Value (SV), Iodine Value (IV), and Unsaponifiable Matter of Some Commodity Oils.

	SE* (g oil/mol KOH)	SV (mg KOH/g oil)	IV (100 × g iodine/g oil)	Unsaponifiable matter (wt%)
butter	242–267	210–232	26–40	<0.5
castor	300–319	176–187	81–91	
coconut	212–226	248–265	6–11	<1.5
corn	288–300	187–195	107–128	1–3
cottonseed	283–297	189–198	100–115	<2
fish**	292–312	180–192	142–176	<2
groundnut (peanut)	286–300	187–196	86–107	<1
lard	276–292	192–203	45–70	<0.2
linseed	286–298	188–196	170–203	<2
olive	286–305	184–196	75–94	<1.5
palm	268–295	190–209	50–55	<1.3
palm kernel	221–244	230–254	14–21	<1
rape***	291–308	182–193	110–126	<0.2
sesame	288–300	187–195	104–120	<2
soybean	288–297	189–195	124–139	<1.5
sunflower	289–298	188–194	118–145	<2
tallow	281–295	190–200	33–47	<0.5

*SE = 56108/SV.
**Cod liver oil.
***Low erucic rape (Canola).
Data from (11).

3. HYDROLYSIS, ESTERIFICATION, AND ESTER EXCHANGE

Reactions converting acids to esters or vice versa and the exchange of ester groups are among the most widely used in fatty acid and lipid chemistry (Figure 4). They find applications from microscale preparation of methyl esters for GC analysis to the industrial production of oleochemicals and biodiesel. The exchange of groups attached to the fatty acid carboxyl is usually an equilibrium process driven to one product by an excess of one reactant or the removal of one product, and it is usually

$$\mathrm{RCOOR'} + \mathrm{H_2O} \rightleftharpoons \mathrm{RCOOH} + \mathrm{R'OH} \qquad (1)$$

$$\mathrm{RCOOH} + \mathrm{R'OH} \rightleftharpoons \mathrm{RCOOR'} + \mathrm{H_2O} \qquad (2)$$

$$\mathrm{RCOOR'} + \mathrm{R''COOH} \rightleftharpoons \mathrm{R''COOR} + \mathrm{RCOOH} \qquad (3)$$

$$\mathrm{RCOOR'} + \mathrm{R''OH} \rightleftharpoons \mathrm{RCOOR''} + \mathrm{R'OH} \qquad (4)$$

$$\mathrm{TAG} + \mathrm{glycerol} \rightleftharpoons \mathrm{MAG} + \mathrm{DAG} \qquad (5)$$

Figure 4. *Exchange reactions at the carboxyl group (1) hydrolysis (Chapter xx), (2) esterification (Chapter xx), (3) acidolysis (Chapter xx), (4) alcoholysis (Chapter xx), and (5) glycerolysis (Chapter xx). The starting ester RCOOR′ will often be a triacylglycerol. MAG—monoacylglycerol; DAG—diacylglycerol; TAG—triacylglycerol.*

carried out with the aid of a catalyst. The catalyst may be an acid, a base, or a lipolytic enzyme. These reactions produce the fatty acids and methyl esters that are the starting point for most oleochemical production. As the primary feedstocks are oils and fats, glycerol is produced as a valuable byproduct. Reaction routes and conditions with efficient glycerol recovery are required to maximize the economics of large-scale production.

There is increasing interest in the use of lipase enzymes for large-scale reactions. Enzyme reactions require milder conditions, less solvent, and give cleaner products—attributes of "green chemistry." Enzymes can exert regio- or stereospecific control over reactions and may also offer a degree of selectivity for particular fatty acids, not observed with acid or base catalysts. Although the reactions of the carboxyl group are normally independent of those of the double bonds in the fatty acid molecule, the presence of a double bond at the $\Delta4$, $\Delta5$, or $\Delta6$ position often results in slower reaction when a reaction is catalyzed by a lipase. Lipase catalyzed reactions are considered in detail below, following a brief description of the reactions involved.

3.1. Hydrolysis

The reaction can be catalyzed by acid, base, or lipase, but it also occurs as an uncatalyzed reaction between fats and water dissolved in the fat phase at suitable temperatures and pressures.

Base catalyzed hydrolysis. Historically, soaps were produced by alkaline hydrolysis of oils and fats, and this process is still referred to as saponification. Soaps are now produced by neutralization of fatty acids produced by fat splitting (see below), but alkaline hydrolysis may still be preferred for heat-sensitive fatty acids.

On a laboratory scale, alkaline hydrolysis is carried out with only a slight excess of alkali, typically 1M potassium hydroxide in 95% ethanol, refluxing for one hour, and the fatty acids recovered after acidification of the reaction mixture. This is a sufficiently mild procedure that most fatty acids, including polyunsaturates, epoxides, and cyclopropenes, are unaltered (19).

Fat splitting. The industrial production of fatty acids uses the direct reaction between water and fats, which proceeds rapidly at ~250°C and 2–6 MPa (20–60 bar). Under these conditions, water is moderately soluble in the oil phase, and stepwise hydrolysis of the triacylglycerols proceeds without the aid of a catalyst. The reaction is carried out with a countercurrent of water that removes the glycerol formed, resulting in ~99% conversion to fatty acids. Glycerol is recovered from the aqueous phase. Sonntag has reviewed industrial fat splitting in detail (20).

3.2. Esterification

Fatty acids are converted to esters by reaction with an excess of alcohol using an acid catalyst or a lipase. For the preparation of methyl esters for GC analysis, boron trifluoride, sulfuric acid, or anhydrous hydrogen chloride in methanol are commonly used (19). Reaction is complete in 30 minutes at reflux. Propyl and butyl esters are prepared in a similar way with the corresponding alcohols. It is not always possible to use an excess of alcohol, for example, in the synthesis of triacylglycerols using a protected glycerol. A more reactive fatty acid derivative such as the acid chloride or anhydride is used, or the fatty acid is reacted directly with the alcohol, using dicyclohexylcarbodiimide (DCC) plus 4-dimethylaminopyridine (DMAP) as a coupling agent, for example, in the synthesis of acylglycerols (21). Some groups in more unusual fatty acids are acid sensitive, for example, epoxides, cyclopropanes, cyclopropenes, and hydroxy compounds, and methods avoiding acids catalysts are needed. Reaction with diazomethane or the less hazardous trimethylsilyl-diazomethane are possibilities (19).

3.3. Ester Exchange Reactions

The fatty acid or alcohol groups present in an ester can be exchanged in a number of ways: by reaction with an excess of other fatty acids (acidolysis), alcohols (alcoholysis), or other esters (interesterification). Generally, the starting point will be a triacylglycerol, and these reactions provide routes by which the composition and properties of oils and fats can be modified.

Acidolysis. This reaction can be acid or enzyme catalyzed and may be used to modify triacylglycerol composition. Acidolysis of an oil containing only C_{16} and C_{18} fatty acids with fatty acids rich in lauric acid (e.g., from palm-kernel oil) results in a triacylglycerol enriched in medium-chain fatty acids.

Alcoholysis. Methanolysis of triacylglycerols is used to prepare methyl esters for fatty acid analysis, a process frequently referred to as transesterification. This can be acid-or base-catalyzed, the method being chosen to avoid modifying acid-or base-sensitive fatty acids and to minimize reaction times. Sterol esters of fatty acids react more slowly than triacylglycerols, and samples containing them require more vigorous reaction conditions. The preparation of methyl esters from oils and fats for GC and GC-MS analysis has been extensively reviewed (19, 22, 23).

Biodiesel is produced on the industrial scale by methanolysis of vegetable oils (usually rape or soybean) or waste fat, particularly using frying oils. Methanolysis proceeds with modest amounts of base catalyst, provided the levels of free fatty acid and water in the oil are low (24, 25). The fatty acid content may be reduced by physical or chemical treatment before methanolysis but for waste fats, alternative processes that do not use base catalysis may be preferred. Lipase catalyzed methanolysis is less sensitive to fatty acid and water in the oil and has been tested in batch (26) and fixed-bed reactor (27) conversion of waste oil and grease to biodiesel.

Glycerolysis, the treatment of triacylglycerols with glycerol and a basic catalyst (sodium hydroxide or sodium methoxide), is used to produce mono- and diacylglycerols on an industrial scale. Molecular distillation is used to produce MAG, which is 90–95% pure and is widely used as an emulsifying agent in foods and other applications.

Interesterification. Interesterification is the intra- and intermolecular exchange of fatty acids on the glycerol backbone of triacylglycerols, although the term is also used more loosely to include acidolysis and other ester exchange reactions. It is applied to either an individual oil or a blend of oils, to produce triacylglycerols with different properties. The molecular species of natural triacylglycerols is not a random mixture of all possible isomers, but it shows greater or lesser selectivity in the distribution of fatty acids between the *sn*-1 and *sn*-3 and the *sn*-2 positions (Table 5). This, as well as the overall fatty acid mixture, determines many of the technically important properties of the oil or fat, for example, solid fat content and melting point. Once subjected to interesterification with a chemical catalyst, the triacylglycerol becomes a random mixture of molecular species. Lipase catalyzed interesterification may alter the distribution of molecular species in a more selective way.

Chemical interesterification (28, 29) is carried out at moderate temperatures (70–100°C), with neat oils and a low concentration ($<0.4\%$) of a base catalyst such as sodium methoxide or ethoxide or Na/K alloy. As the catalyst is destroyed by water and free fatty acids, the oil must be carefully refined and dried before adding the catalyst. Reaction proceeds through sequential fatty acid exchange reactions, following formation of what is believed to be the true catalyst, the alkali metal derivative of a diacylglycerol. There is no observed selectivity for fatty acid or glycerol position, leading to a fully random product. The product composition can be controlled through directed interesterification at lower temperatures. Na/K alloy is used as catalyst as it is active at temperatures below 50°C and cooling the reaction mixture causes high melting trisaturated triacylglycerols to crystallize out, altering the composition of the liquid phase in which reaction occurs. The remaining liquid phase is randomized by further reaction and high melting products continue to crystallize out, eventually leading to solid and liquid products richer in trisaturated and triunsaturated species than the fully randomized fat (29).

Interesterification is used to modify fat properties without recourse to partial hydrogenation. Hardened fats produced by partial hydrogenation contain *trans*-isomers, which are now regarded as undesirable by nutritionists and will be increasingly subject to product labeling regulations. Liquid fats can be hardened by interesterification with fully saturated fats (either stearin fractions or fully hydrogenated oils), raising the solid fat content without isomerizing any of the fatty acids. The use of interesterification to produce margarine and spreads has increased recently, particularly in Europe.

3.4. Lipase Catalyzed Reactions

Lipases are enzymes that hydrolyze fatty acids from lipid species (e.g., triacylglycerols or phospholipids) in vivo. A number of lipases, mainly of bacterial origin, are now available immobilized onto a solid support for use as industrial scale catalysts.

Immobilized lipases catalyze the whole range of ester exchange reactions described above (alcoholysis, acidolysis, esterification) as well as hydrolysis. There are two significant differences between lipase and chemically catalyzed reactions. First, lipase catalyzed reactions take place at a lower temperature and with fewer side reactions, leading to cleaner products: an environmentally friendly alternative to some existing processes. Second, enzyme catalyzed reactions are more selective, offering control over reactions not possible with a chemical catalyst. Selectivity may be for fatty acids at different positions on the glycerol backbone (*sn*-1 and *sn*-3 rather than *sn*-2) or for particular fatty acids, discriminating by double-bond position or chain length (30, 31). The widely studied Lipozyme RM IM (*Rhizomucor miehei* lipase immobilized onto a weak anion exchange resin) preferentially hydrolyzes short-chain acids relative to medium and long chains from triacylglycerols. Hydrolysis at the *sn*-1 position is somewhat faster than at *sn*-3, and hydrolysis at *sn*-2 is very slow (31).

Lipase catalyzed reactions take place in the neat oil or in a nonpolar (usually hydrocarbon) solvent. The efficiency depends on the amount of water, solvent (if present), temperature, and ratio of reactants. A factorial approach can be used to optimize the conditions (32). In interesterification reactions, 1,3-specific enzymes give control over product composition that is not possible using chemical catalysts. For example, starting with SOS and OOO, chemical interesterification produces all eight possible isomers (see Table 5). Enzymatic interesterification does not exchange fatty acids at the *sn*-2 position, and it will result in only two additional molecular species, OOS and SOO. In more realistic situations, chemical and enzymatic interesterification may produce the same or a similar number of molecular species, but in different proportions (31).

Enzymatic interesterification has most potential for high-value products such as confectionary fats and nutritional products, for example, cocoa butter equivalents prepared from cheap and readily available starting materials. Acidolysis of palm mid fraction, rich in POP, with stearic acid gives a cocoa butter equivalent rich in POSt and StOSt, through exchange at the *sn*-1 and *sn*-3 positions while retaining the oleate at the *sn*-2 position. Tripalmitin treated similarly with oleic acid gives products where the palmitate is retained at the *sn*-2 position, whereas oleate is introduced at *sn*-1 and *sn*-3, producing a human milk fat substitute such as Betapol. In practice, pure starting materials are not used. Feedstocks rich in tripalmitin and oleic acid are reacted in a two step-process: alcoholysis to *sn*-2- monoacylglycerols followed by esterification (33).

Both batch and fixed-bed reactors have been used and tested on the near ton scale (34) for the production of high-value fats. This technology has now progressed to pilot production, using a 1-m^3 fixed-bed plug-in reactor containing the immobilized enzyme Lipozyme TL IM (35). Blends of palm oil or stearin with palm-kernel or coconut oil are interesterified in less than one hour at 70°C, and no downstream processing is required as the enzyme is retained in the reactor. This is a practical, lower energy alternative to hydrogenation and chemical interesterification, free from the *trans*-isomer production of the former and more selective and "natural" than the latter.

Lipases also discriminate between fatty acids with different double-bond positions. The reaction of fatty acids with Δ4, Δ5, and Δ6 double bonds is significantly slower than Δ9 acids when catalyzed by some enzymes. This is illustrated by some examples of attempts to concentrate γ-linolenic acid (GLA; 18:3 6*c*9*c*12*c*) from borage oil. Hydrolysis of borage oil with *Candida rugosa* lipase resulted in selective hydrolysis of the Δ9 acids (mainly 18:2) increasing the amount of GLA in the remaining acylglycerols (36). The efficiency of the enrichment was influenced by the initial triacylglycerol composition and the extent of hydrolysis. Starting with a borage oil containing 22% GLA, the upper limit of enrichment was to 46%, but higher values resulted from repeated hydrolysis of the recovered acylglycerols. A two-step sequence involving both enzymatic hydrolysis and re-esterification achieved higher enrichment (37). Nonselective hydrolysis with *Pseudomonas* sp. lipase was optimized for high GLA recovery (93%). Esterification with lauryl alcohol, using *Rhizopus delemar* lipase, discriminated strongly against GLA, resulting in enrichment in the unesterified fatty acids from 22.5% to 70.2% with a recovery efficiency of 75.1%. A 92.1% GLA concentrate, obtained by low-temperature crystallization of borage oil fatty acids, was enriched to 99.1% by esterification with butanol, catalyzed by Lipozyme IM-60 (38).The overall recovery was 72.8%. The operating parameters (alcohol, concentration, temperature, and solvent) were systematically investigated.

Eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), Δ5 and Δ4 acids respectively, are discriminated against during lipase catalyzed reactions and reaction of DHA may be significantly slower than EPA. Alcoholysis of tuna oil ethyl esters with lauryl alcohol using *Rhizomucor miehei* lipase enriches the DHA in the unreacted ethyl esters, whereas the concentration of EPA is simultaneously reduced (39). A concentrate containing 60% DHA and 8.6% EPA was alcoholyzed with excess lauryl alcohol (1:7 mole ratio). The remaining ethyl esters contained 93% DHA in 74% recovery, and EPA was reduced to 2.9%. Both nonregiospecific and *sn*-1,3-specific enzymes incorporate GLA into seal blubber and menhaden oil (3:1 mole ratio of GLA to triacylglycerol) producing an oil rich in both n-3 and n-6 polyenes (40). The highest incorporation was with the nonspecific enzyme.

4. OXIDATION

The fatty acid alkyl chain is susceptible to oxidation both at double bonds and adjacent allylic carbons. Free-radical and photooxidation at allylic carbons are responsible for deterioration of unsaturated oils and fats, resulting in rancid flavors and reduced nutritional quality, but they are also used deliberately to polymerize drying oils. Oxidation of double bonds is used in oleochemical production either to cleave the alkyl chain or to introduce additional functionality along the chain. Enzyme catalyzed oxidation is the initial step in the production of eicosanoids and jasmonates (biologically active metabolites in animals and plants respectively) but is not discussed further here.

4.1. Autoxidation and Photooxidation

Both autoxidation and photooxidation produce allylic hydroperoxides from unsaturated centers.

$$\sim\!\sim\mathrm{CH{=}CH{-}CH_2}\sim\!\sim \;+\; \mathrm{O_2} \longrightarrow \;\sim\!\sim\mathrm{CH{=}CH{-}CH(OOH)}\sim\!\sim$$

During this process, the position and geometry of the double bond may change. The hydroperoxide mixtures produced by autoxidation and photooxidation are not the same, indicating that different mechanisms are involved. Free radical oxidation can be promoted or inhibited. Deliberate promotion speeds the polymerization of drying oils, and strenuous efforts are made to inhibit the onset of rancidity in edible oils. Frankel has recently reviewed this topic in depth (41); see also (1) for an extensive discussion of oxidation of food lipids.

4.1.1. Autoxidation

Autoxidation is a free-radical chain reaction, involving a complex series of reactions that initiate, propagate, and terminate the chain.

initiation	$RH \rightarrow R^\bullet$	
propagation	$R^\bullet + O_2 \rightarrow ROO^\bullet$	fast
	$ROO^\bullet + RH \rightarrow ROOH + R^\bullet$	rate determining
termination	$R^\bullet$, $ROO^\bullet \rightarrow$ stable products	

The chain reaction is initiated by abstraction of an allylic hydrogen to give an allylic radical stabilized by delocalization over three or more carbons. The initiator is a free radical, most probably produced by decomposition of hydroperoxides already present or produced by photooxidation. The decomposition may be thermal, but it is more likely promoted by traces of variable redox state metal ions. Autoxidation is characterized by an induction period during which the concentration of free radicals increases until the autocatalytic propagation steps become dominant. During the induction period, there is little increase in oxidation products.

The first step of the propagation sequence is reaction of the allylic radical with molecular oxygen, producing a peroxy radical. This step is much faster than the subsequent abstraction of another allylic hydrogen by the peroxy radical, producing both an allylic hydroperoxide and a new allylic radical that continues the chain reaction. Hydrogen abstraction is the rate-determining step and is therefore selective for the most readily abstracted hydrogen. Methylene-interrupted dienes and polyenes, where the allylic radical can be delocalized over five carbons, are oxidized faster than monoenes where the radical is delocalized over three carbons (Figure 5).

The chain reaction is terminated by reactions that remove radicals that would otherwise produce more allylic radicals by hydrogen abstraction. Examples are the combination of two hydroperoxy radicals leading to nonradical products and molecular oxygen or reaction with a free-radical scavenger (antioxidant) generating a more stable radical.

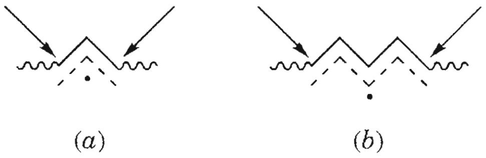


Figure 5. *Allylic radicals produced during autoxidation. (a) Those from isolated double bonds are delocalized over three carbons. (b) Those from methylene-interrupted dienes or polyenes are delocalized over five carbons. The arrows show the site of attachment of O_2 giving a peroxy radical.*

The rate of autoxidation generally increases with increasing unsaturation. Linoleate, as neat methyl or ethyl ester, reacts approximately 40 times faster than oleate, and for higher polyenes, the rate doubles for each additional double bond (42). Trilinolein does not follow the same kinetics as the simple esters and oxidizes somewhat faster. The medium also influences susceptibility to oxidation, and these generalizations may not hold in emulsified systems (e.g., many food formulations) where oxidation occurs at the interface between aqueous and fat phases (43). In aqueous micelles, EPA and DHA are unexpectedly stable (44), oxidizing much more slowly than linoleate. In one experiment, over half the linoleate was oxidized within 50 hours and ~90% of EPA and DHA was still present after 2000 hours. The stability of the higher polyenes is attributed to their tightly coiled configuration in the aqueous medium, making attack by oxygen or free radicals more difficult.

Mechanistic studies of autoxidation have concentrated on methylene-interrupted fatty acids, but many of the observations are valid for other compounds. Conjugated fatty acids such as CLA also oxidize through an autocatalytic free radical reaction, with the predominant hydroperoxide determined by the geometry of the conjugated diene system (45). Other groups with activated methylenes may be susceptible to oxidation, for example, the ether methylenes of ethoxylated alcohols used as surfactants (46).

4.1.2. Photooxidation

Light, in the presence of oxygen, promotes oxidation of unsaturated fatty acids. Ultraviolet radiation decomposes existing hydroperoxides, peroxides, and carbonyl and other oxygen-containing compounds, producing radicals that initiate autoxidation (42). Photooxidation by longer wavelength near ultraviolet or visible light requires a sensitizer. Naturally present pigments such as chlorophyll, hematoporphyrins, and riboflavin act as sensitizers as do dyes, including erythrosine and methylene blue. Light excites these sensitizers to the triplet state that promotes oxidation by type I and type II mechanisms. Unlike autoxidation, there is no induction period.

In type I photosensitized oxidation, the triplet state sensitizer abstracts a hydrogen or electron from the unsaturated oil, producing radicals that initiate chain propagation as in autoxidation. However, chain-breaking antioxidants do not stop this reaction as new radicals are produced photochemically. In type II photooxidation, the energy of the triplet sensitizer is transferred to molecular oxygen, converting it

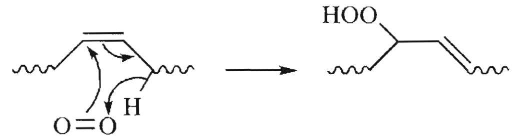


Figure 6. *Ene reaction between singlet oxygen and an olefinic bond. The hydroperoxide may be attached to either of the inital double bond carbons.*

to its excited singlet state. Singlet oxygen is highly electrophilic and reacts rapidly with olefins in an ene reaction, producing allylic hydroperoxides with oxygen attached to one of the original olefinic carbons and the shifted double bond now *trans* (Figure 6).

The ene reaction differs from free-radical oxidation, where oxygen attaches to an outer carbon of the delocalized allylic radical (Figure 5), resulting in a different mixture of hydroperoxides. For example, photooxidation of linoleate produces four isomers: 9-OOH,10*t*12*c*, 10-OOH,8*t*12*c*, 12-OOH,9*c*13*t*, and 13-OOH,9*c*11*t*. The same 9- and 13-hydroperoxides are produces by autoxidation, but the 10- and 12-hydroperoxides are only produced by photooxidation.

Photooxidation is much faster than autoxidation; the reaction of linoleate with singlet oxygen is approximately 1500 times faster than that with triplet oxygen (47). There is less difference in the rate of photooxidation between monoenes and polyenes than is seen in autoxidation. The relative rates for oleate, linoleate, linolenate, and arachidonate are 1.0, 1.7, 2.6, and 3.1 (48, 49). This contrasts with the 40-fold increase in rate of autoxidation between oleate and linoleate.

4.1.3. Decomposition of Hydroperoxides Allylic hydroperoxides are reactive molecules and decompose readily in a complex series of reactions, the course of which depends on the medium and other conditions (1, 41). Cleavage between the oxygens is energetically favored, leading to alkoxy and hydroxyl radicals. Redox metal ions such as Fe^{2+}/Fe^{3+} and Cu^{+}/Cu^{2+} are particularly effective catalysts. The resulting radicals can initiate further autoxidation and produce a number of stable products, many with undesirable nutritional and flavor properties (Figure 7). Products with the same chain length as the alkoxy radical include epoxides, ketones, and hydroxy fatty acids. The significant products producing off-flavors are those resulting from chain scission β to the alkoxy radical, producing shorter chain aldehydes and hydrocarbons. Alkadienals have particularly low-odor thresholds and a few parts per billion of nonadienals from n-3 fatty acids are responsible for a marked fishy taint even when other signs of oxidation are absent (50).

There are a number of analytical measures of oxidative deterioration of oils and fats. The most widely used are the peroxide value (PV) (15), which measures the hydroperoxide content by iodine titration and the anisidine value (AV) (15), which detects aldehydes by a color reaction. As an oil suffers damage because of autoxidation, the hydroperoxide content, and PV rise but do not do so indefinitely. As the hydroperoxides break down, the concentration of aldehydes and AV increase. Oxidation is better assessed by a combination of PV and AV, the Totox value

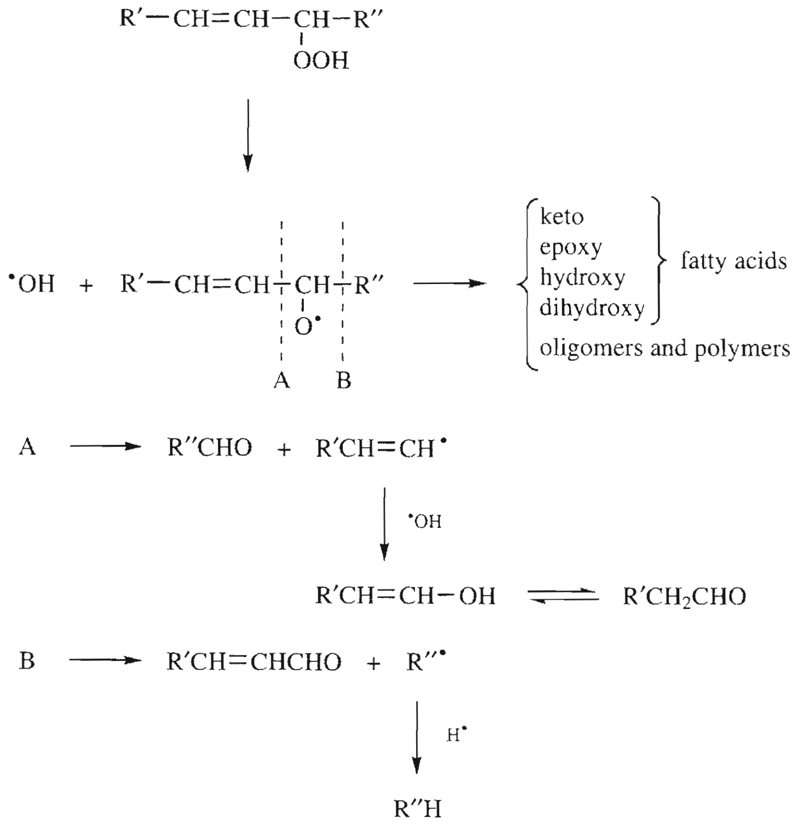


Figure 7. *Decomposition reactions of allylic hydroperoxides.*

($= 2 \times \mathrm{PV} + \mathrm{AV}$) being a better index of oxidation than either PV or AV alone. Volatile products can be removed from oils by deodorization, but aldehydes attached to the carboxyl end of the chain remain part of the triacylglycerol (sometimes called "core" aldehydes) and are indicators of previous oxidative damage.

4.1.4. Antioxidants Lipid oxidation is influenced by many factors: the medium, oxygen concentration, temperature, light, degree of unsaturation, and metal ions among others. In the presence of oxygen, oxidation cannot be entirely prevented nor can it be reversed, but it can be inhibited, delaying the buildup of oxidized products to unacceptable levels. Antioxidants can interact with several steps of free-radical or photooxidation. Their performance is medium and concentration dependent and requires care as they can also act as prooxidants under some conditions (51).

The most widely used antioxidants are free radical scavengers that remove reactive radicals formed in the initiation and propagation steps of autoxidation. A number of natural or synthetic phenols can compete, even at low concentrations, with lipid molecules as hydrogen donors to hydroperoxy and alkoxy radicals, producing hydroperoxides and alcohols and an unreactive radical. β-carotene reacts with peroxy radicals, producing a less-reactive radical. These stabilized radicals do not initiate or propagate the chain reaction.

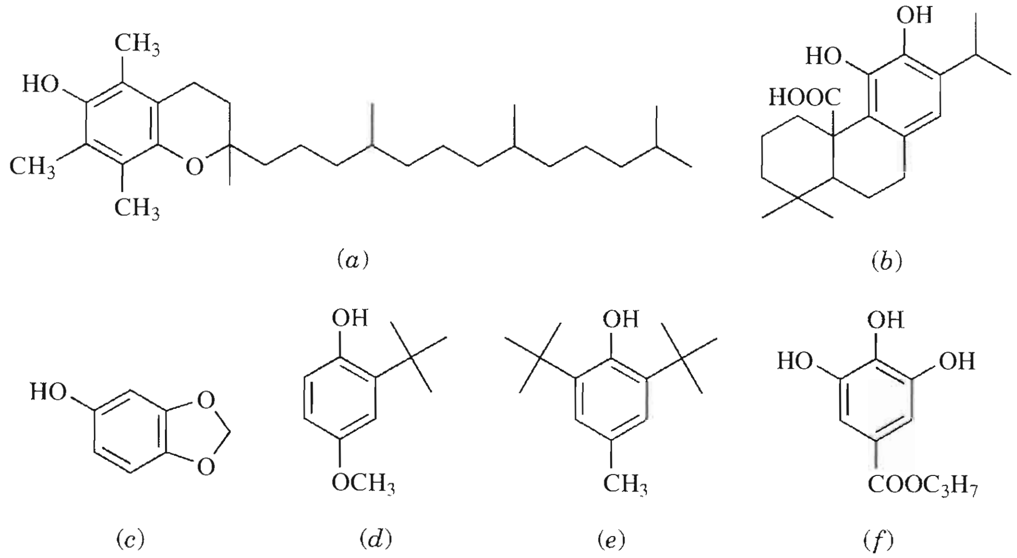


Figure 8. *Natural antioxidants (a) α-tocopherol, (b) carnosic acid, and (c) sesamol. Synthetic antioxidants (d) butylated hydroxyanisole (BHA), (e) butylated hydroxytoluene (BHT), and (f) propyl gallate.*

Tocopherols are phenolic antioxidants (Figure 8) naturally present in most plant oils (see Chapter X). They are concentrated in the distillate from physical refining, which results in a corresponding decrease in the refined oil. Soybean distillate is a source of tocopherols for antioxidant formulations. Carnosic acid (Figure 8) is isolated from rosemary and other herbs. Sesamol (Figure 8) is a characteristic antioxidant of sesame oil, responsible for its high stability (Chapter xx). Synthetic antioxidants are monocyclic phenols with highly branched substituents (Figure 8). In all of these compounds, the radicals formed by abstraction of the phenolic hydrogen are highly delocalized and unreactive. The antioxidant action of free-radical scavengers is sacrificial, delaying oxidation until the antioxidant is used up. Oxidized tocopherols may be regenerated by ascorbic acid, extending their effective life while keeping their concentration below prooxidant levels.

Photooxidation is not inhibited by free-radical scavengers. Natural pigments that act as sensitizers may be reduced during refining, increasing stability. Singlet oxygen and excited state sensitizers can be deactivated either by competitive reaction or physical energy transfer, for example, to β-carotene. Tocopherols and some amines also act as singlet oxygen quenchers through physical energy transfer.

Redox metal ions, particularly iron and copper, react with hydroperoxides, initiating further autoxidation and producing undesirable decomposition products. Complete removal of these metal ions is not possible, but steps can be taken to reduce their effect. Chelating agents such as EDTA, citric acid, phosphate, and polyphosphates may reduce the effective metal ion concentration. Their efficacy depends on pH, and they may also show prooxidant activity. The role of metal ions in hydroperoxide decomposition in food emulsions has been reviewed recently (52).

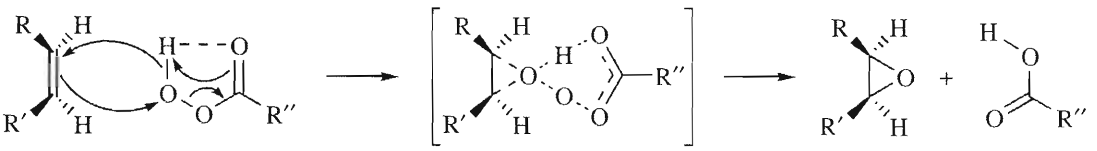


Figure 9. Epoxidation mechanism proposed by Bartlett (53). The cis-olefin gives rise to a cis-epoxide.

4.2. Epoxidation

Epoxides are produced by reaction of double bonds with peracids. This proceeds by a concerted mechanism, giving *cis* stereospecific addition (Figure 9) (53). Thus, a *cis* olefin leads to a *cis* epoxide and a *trans* olefin to a *trans* epoxide. The order of reactivity of some peracids is *m*-chloroperbenzoic > performic > perbenzoic > peracetic; electron withdrawing groups promote the reaction. The carboxylic acid produced is a stronger acid than the strongly hydrogen bonded peracid and may lead to subsequent ring opening reactions especially in the case of formic acid. Small scale reactions are carried out with *m*-chloroperbenzoic acid in a halocarbon or aromatic solvent, in the presence of bicarbonate to neutralize the carboxylic acid as it is formed (54, 55).

Oils, mainly soybean but also linseed, are epoxidized on an industrial scale (100,000 tons per year) as stabilizers and plasticizers for PVC. The reactive epoxide groups scavenge HCl produced by degradation of the polymer. Epoxidation is carried out with performic or peracetic acid produced in situ from formic or acetic acid and high strength hydrogen peroxide (70% w/w). Peracids are unstable, and the reaction is exothermic. The concentration of peracid is kept low by using a low concentration of the carboxylic acid either in the neat oil or in a hydrocarbon solvent. The carboxylic acid is regenerated after epoxidation. Complete epoxidation is not achieved as in the acidic medium ring opening reactions occur producing dihydroxy and hydroxy carboxylates as byproducts.

Recent studies have attempted to improve the efficiency of epoxidation under milder conditions that minimize the formation of byproducts. Chemo-enzymatic epoxidation uses the immobilized lipase from *Candida antartica* (Novozym 435) (56) to catalyze conversion of fatty acids to peracids with 60% hydrogen peroxide. The fatty acid is then self-epoxidized in an intermolecular reaction. The lipase is remarkably stable under the reaction conditions and can be recovered and reused 15 times without loss of activity. Competitive lipolysis of triacylglycerols is inhibited by small amounts of fatty acid, allowing the reaction to be carried out on intact oils (57). Rapeseed oil with 5% of rapeseed fatty acids was converted to epoxidized rapeseed oil in 91% yield with no hydroxy byproducts. Linseed oil was epoxidized in 80% yield. Methyl esters are also epoxidized without hydrolysis under these conditions.

Methyltrioxorhenium (MTO) catalyses direct epoxidation by hydrogen peroxide. The reaction is carried out in pyridine, avoiding acidic conditions detrimental to high epoxide yield and uses less concentrated hydrogen peroxide (30%) than other methods (58). This method epoxidized soybean and metathesized (see Section 7.4)

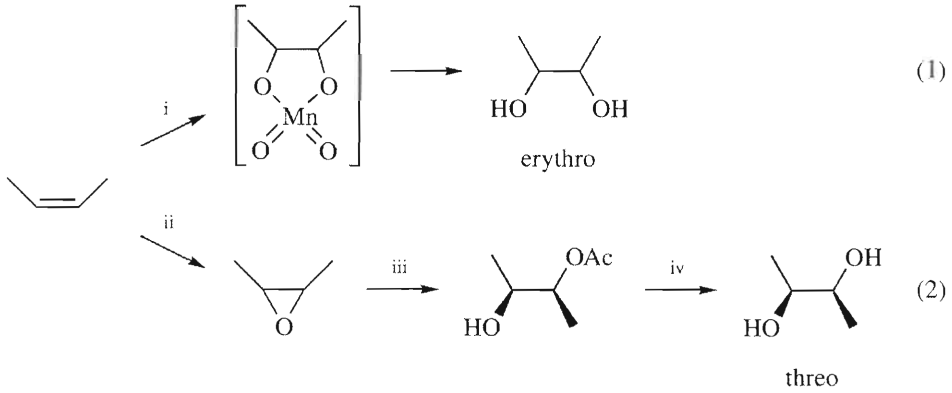


Figure 10. *Stereochemistry of hydroxylation reactions: (1) with dilute alkaline permanganate and (2) through epoxide ring opening. (i) $KMnO_4$, NaOH; (ii) m-chloroperbenzoic acid, $NaHCO_3$, CH_2Cl_2; (iii) CH_3COOH; (iv) base catalyzed hydrolysis.*

soybean oil in high yield (59). The epoxidized metathesized oil was more stable to polymerization than that produced using *m*-chloroperbenzoic acid, presumably because it was free of acidic impurities. These and other novel approaches to epoxidation have recently been reviewed (4, 60, 61). None has yet found industrial application.

Epoxides are reactive and readily ring open in acid, following protonation of the epoxy oxygen (Figure 10). This is a route to diols (see Section 4.3), polyols used in polymer production and a range of α-hydroxy compounds. Ring opening of methylene-interrupted diepoxides leads to 5 and 6 membered ring ethers through neighboring group participation (7).

4.3. Hydroxylation

Double bonds are converted to monohydroxy derivatives by acid catalyzed addition of carboxylic acids, followed by hydrolysis. The carbocation intermediate is prone to rearrangement, leading to a mixture of positional isomers. Hydroboration with borane:1,4-oxathiane followed by alkaline hydrolysis a regioselective reaction (62) has been used to prepare hydroxy fatty acids as GC-MS standards in high yield (63).

Hydroxylation reactions leading to diols have much in common with epoxidation and oxidative cleavage reactions (see Section 4.4), the end product depending on the strength of the oxidizing agent. Dilute alkaline permanganate or osmium tetroxide react through cyclic intermediates resulting from *cis* addition of the reagent giving an *erythro* diol. Ring opening epoxides with acid is a *trans* addition, leading to a *threo* product (Figure 10).

An oxygen bridged manganese complex was recently reported to catalyze double-bond oxidation by hydrogen peroxide leading to a mixture of epoxide, *cis*-diol, and hydroxy ketone products (64). This is an interesting model reaction for the efficient use of hydrogen peroxide as a cheap hydroxylating agent if the selectivity can be improved. A number of microorganisms are reported to produce a range of novel di- and trihydroxy fatty acids and are being investigated as potential biocatalysts (65).

4.4. Oxidative Cleavage

Double bonds are cleaved by a number of oxidizing agents, converting the olefinic carbons to carboxylic acids, aldehydes, or alcohols. Fatty acids give a monofunctional product from the methyl end and a difunctional product from the carboxyl end (along with low-molecular-weight products from methylene-interrupted systems).

Although now largely superceded by GC and GC-MS methods for structure determination, oxidative cleavage with ozone or permanganate/periodate and identification of the resulting products is a powerful method for double-bond location, particularly for monoenes (19). Reaction with alkaline permanganate/periodate proceeds through the diol resulting from reaction with dilute permanganate (see Section 4.3). The diol is split into two aldehydes by reaction with periodate, and the aldehydes are subsequently oxidized to carboxylic acids by permanganate. Alternatively, diols derived from double bonds are cleaved to aldehydes by lead tetraacetate or periodate.

Ozone reacts directly with double bonds under mild conditions and is the preferred degradative method for double-bond location (19). The reaction occurs in several steps (64), starting with a 1,3-dipolar cycloaddition (Figure 11). The addition product decomposes rapidly into an aldehyde and a carbonyl oxide. In the absence of solvent or in nonparticipating solvents, these recombine forming a relatively stable 1,2,4-trioxolane or ozonide. The separation into aldehyde and carbonyl oxide during this rearrangement is supported by production of six ozonide species from unsymmetrical olefins. Ozonides can be converted to a number of stable products; oxidation yields carboxylic acids, mild reduction gives aldehydes, and treatment with nickel and ammonia gives amines providing useful synthetic routes to difunctional compounds from fatty acids [e.g., Furniss et al. (67)]. In a carboxylic acid or alcohol solvent, the carbonyl oxide reacts with the solvent producing mainly

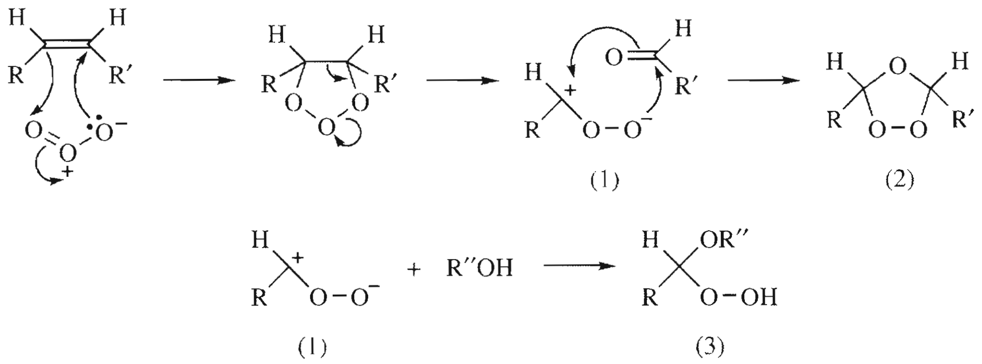


Figure 11. Ozonolysis reaction mechanism. In nonparticipating solvents, the carbonyl oxide (1) and aldehyde recombine to give the moderately stable ozonide (2). Hydroperoxides (3) are formed in protic solvents, and R″ can be alkyl or acyl.

acyloxy or alkoxyhydroperoxides, respectively, along with other more complex products (68). These hydroperoxides are oxidized or reduced to the same products as the ozonides.

Ozonolysis is the only oxidative cleavage that is used industrially. Around 10,000 tons per year of azelaic acid (nonane-1,9-dioic acid) are produced along with pelargonic acid (nonanoic acid) by ozonolysis of oleic acid. Azelaic acid is used for polymer production and is not readily available from petrochemical sources. Other dibasic acids potentially available by this route are brassylic (tridecane-1,13-dioc) and adipic (hexane-1,6-dioic) acids from erucic (22:1 13*c*) and petroselenic (18:1 6*c*) acids, respectively. High-purity monoenes are required as feedstock to avoid excessive ozone consumption and byproducts. Ozonolysis is a clean reaction, carried out at low temperatures without catalyst. However, ozone is toxic and unstable, as are the intermediates. Industrial scale ozonolysis is carried out in pelargonic acid run countercurrent to ozone at 25–45°C followed by decomposition at 60–100°C in excess oxygen (69). Ozone must be generated continuously on-site by electrical discharge in air, and ozone production is the limiting factor for large-scale production (70).

Ruthenium oxide (RuO_4) catalyzes oxidative cleavage of oleic acid to pelargonic and azelaic acids efficiently in the presence of NaOCl as an oxygen donor to regenerate Ru(VIII) (71). However, the production of halogen salt byproducts makes this impractical for large-scale production. Hydrogen peroxide and peracetic acid are cheaper and more environmentally benign oxidants, the byproduct from reaction or regeneration of peracid being water, but give very low yields with RuO_4. Ruthenium(III) acetylacetonate ($Ru(acac)_3$) with peracetic acid or Re_2O_7 with hydrogen peroxide give moderate yields with internal double bonds, but ~80% conversion with terminal olefins. Terminal olefins, produced from fatty acids with an internal double bond by metathesis with ethylene, are converted to dibasic acids without

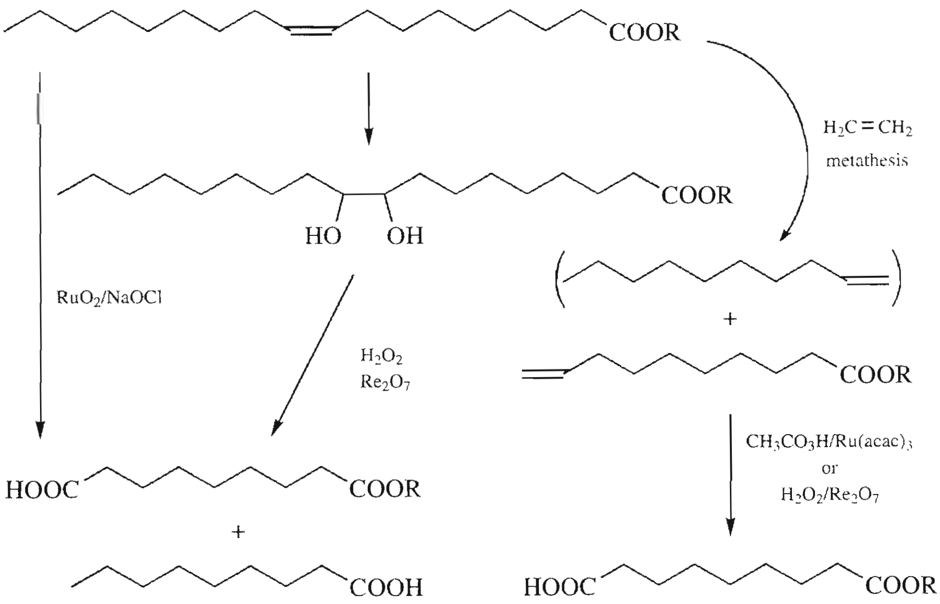


Figure 12. *Alternative oxidative cleavage reactions.*

concomitant production of monobasic acids. Diols produced by hydroxylation are cleaved by Re_2O_7 with hydrogen peroxide to di- and monobasic acids (Figure 12). These reactions offer an alternative to ozonolysis for the production of dibasic acids, but they have still to be optimized for industrial application (71, 72).

5. REDUCTION

Both carbon–carbon double bonds and the carboxyl group of fatty acids can be reduced, either together or separately depending on the reaction conditions. Catalytic reduction is an important industrial route to hardened fats, fatty alcohols, and fatty amines, using well-established technologies.

5.1. Hydrogenation of Double Bonds

Transition metals such as Co, Ni, Cu, Ru, Pd, and Pt catalyze hydrogenation of double bonds. Palladium on charcoal or Adam's catalyst (platinum oxide) promote saturation of fatty acids at ambient temperature and hydrogen pressure. Hydrogenation is accompanied by exchange and movement of hydrogen atoms along the chain in the region of the double bonds, demonstrated by the large number of isotopomers formed on deuteration. Homogeneous deuteration with Wilkinson's catalyst (tris (triphenylphosphine)rhodium(I) chloride) proceeds without hydrogen movement or exchange (73) and in conjunction with GC-MS analysis is used to locate double bonds. Partial hydrogenation with hydrazine does not isomerize unreacted double bonds and is useful for structural analysis of polyenes and was recently used to examine long-chain metabolites of conjugated linoleic acid (CLA) (74).

5.2. Catalytic Partial Hydrogenation

Partial hydrogenation reduces the polyene content of oils while maintaining or increasing the monoene content. Reduction of double bonds is accompanied by a variable degree of *cis*-to *trans*-isomerization. "Brush" hydrogenation of soybean or rape oil reduces linolenic content, improving oxidative stability, whereas more extensive hydrogenation increases solid fat content, producing "hardened" fats for spreads and shortenings. Partial hydrogenation has been used for the past century, in margarine production and remains an important process for edible fat modification (Chapter xx) despite concerns about adverse nutritional properties of *trans*-fatty acids. There are recent reviews of the mechanism (75, 76) and technology (77).

A number of uncertainties remain about the mechanism of the reaction and the factors controlling selectivity between polyenes and monoenes, and the balance between hydrogenation and isomerization. Hydrogenation is a three-phase reaction among liquid oil, gaseous hydrogen, and solid catalysts carried out as a batch process in autoclaves to maintain consistent products. Temperature, hydrogen pressure, amount and formulation of catalyst, and agitation are all carefully controlled.

Supported nickel is invariably used as catalyst. Although other catalysts are equally or more effective, nickel has widespread acceptance from long use, ease of removal, and low cost. Unremoved traces of other metals such as copper might also reduce the oxidative stability of the product.

The reaction mechanism must account for the selectivity of the reaction (polyenes reacting faster than monoenes) and the production of *trans*-monoenes. Hydrogen addition is in two steps with a semihydrogenated intermediate. Addition of the first hydrogen is reversible, regenerating a double bond with potentially altered position or geometry. Addition of a second hydrogen irreversibly produces a saturated bond (Figure 13). Dijkstra (76) proposed that for dienes, the formation of the semihydrogenated intermediate is rate determining and hydrogen concentration dependent, whereas for the conversion of monoene to saturate, the rate-determining and hydrogen concentration-dependent step is the addition of the second hydrogen. At low dissolved hydrogen concentrations, isomerization of monoenes is favored over saturation, allowing control of the product composition by hydrogen pressure, agitation, and reaction time.

Copper catalysts show different selectivity compared with nickel. Copper only catalyzes hydrogenation of methylene-interrupted systems, showing high selectivity for polyenes and no reaction with oleate or other monoenes produced by reduction of polyenes. The first step is production of conjugated dienes that are the species hydrogenated. Dijkstra recently reassessed this reaction, suggesting removal of an allylic hydrogen as the first step in production of the conjugated diene (78).

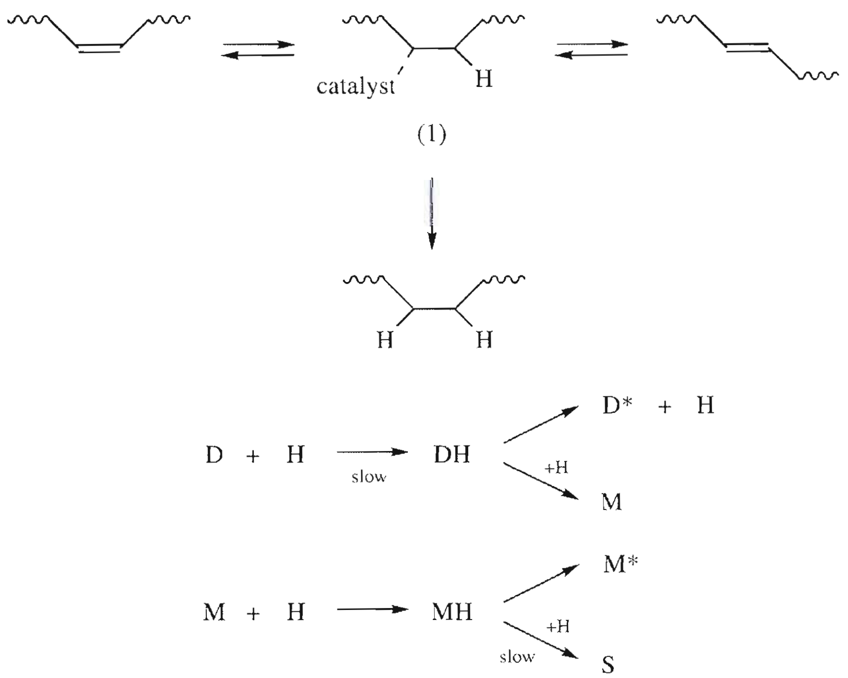


Figure 13. *Partial hydrogenation. The partially hydrogenated intermediate (1) may lead to cis or trans unsaturated or saturated products. D—diene; M—monoene; S—saturate;* * *potentially isomerized. Formation of M* is favored at a low hydrogen concentration.*

5.3. Production of Fatty Alcohols

Triacylglycerols, fatty acids, and esters can be reduced to aldehydes, alcohols, or hydrocarbons, the main application being the production of fatty alcohols. On a small scale, lithium aluminum hydride (in excess of stochiometric requirement) is a convenient reducing agent for the carboxyl group without affecting polyunsaturated chains. Industrially, catalytic hydrogenation is used and has been reviewed (79, 80).

Long-chain alcohols are produced from both oleochemical and petrochemical sources. Oils and fats provide straight chain lengths not readily available otherwise and the possibility of unsaturated chains. The main feed stocks are coconut and palm-kernel oil for C_{12}–C_{14} alcohols and technical grades of tallow and palm oil for C_{16}–C_{18} alcohols. The preferred starting material for catalytic hydrogenation is methyl ester. Fatty acids are corrosive and need harsh reaction conditions, leading to unwanted byproducts. Reduction of intact oils leads to loss of glycerol, a valuable byproduct, through over-reduction to propane diol and propanol, as well as excessive hydrogen and catalyst consumption. Methyl esters are reduced to saturated alcohols with copper chromite catalyst (~2%) at 250–300°C and 25–30-MPa (250–300 bar) hydrogen in a suspension system or at 200–250°C with a fixed-bed catalyst. The methanol produced is recycled for methyl ester production. Zinc-based catalysts do not hydrogenate double bonds and are used to produce unsaturated alcohols such as oleyl alcohol.

6. PRODUCTION OF SURFACE ACTIVE COMPOUNDS AND OLEOCHEMICALS

The main non-food use of oils and fats is the production of surfactants. The amphiphilic properties of fatty acids, exploited for centuries in the use of soaps, can be modified by changing the carboxyl group into other hydrophilic groupings, giving anionic, cationic, amphoteric, and nonionic surfactants. There is also scope for functionalizing the aliphatic chain, but this has not been widely used commercially. The chain length of the feed stock, C_{12}–C_{14} from lauric oils, C_{22} from high erucic rape and fish oils, and C_{16}–C_{18} from most other sources, can be used to modify solubility. The main starting materials for surfactant production are fatty acids and alcohols with a range of N-containing derivatives produced through amides and amines. Surfactants of oleochemical origin may biodegrade better than petrochemical products, giving an environmental benefit in addition to being derived from renewable resources. Recently, surfactants have been produced from fully renewable resources. Oleochemical surfactant production has been reviewed (81–85).

6.1. Nitrogen-Containing Compounds

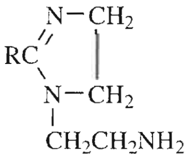
The presence of nitrogen, either in a neutral or cationic group, gives surfactant properties that are not easily produced with other compounds. A diverse range of nitrogen-containing compounds are produced, for which the starting point is an

TABLE 7. Routes to Nitrogen-Containing Surfactants.

	Product
$RCH_2NH_2 + CH_2O \rightarrow$ (reduction) $\rightarrow RCH_2NMe_2$	tertiary amine
$RCH_2CONMe_2 \rightarrow$ (reduction) $\rightarrow RCH_2NMe_2$	tertiary amine
$RCH_2OH + Me_2NH \rightarrow$ (catalytic hydrogenation) $\rightarrow RCH_2NMe_2$	tertiary amine
$ROH + CH_2{=}CHCN \rightarrow RO(CH_2)_2CN \rightarrow$ (reduction) $\rightarrow RO(CH_2)_3NH_2$	etheramine
$RNH_2 + CH_2{=}CHCN \rightarrow RNH(CH_2)_2CN \rightarrow$ (reduction) $\rightarrow RNH(CH_2)_3NH_2$	diamine
$RNH(CH_2)_3NH_2 + CH_2{=}CHCN \rightarrow RNH(CH_2)_3NH(CH_2)_2CN \rightarrow$ (reduction) $\rightarrow RNH(CH_2)_3NH(CH_2)_3NH_2$	triamine
$RO(CH_2)_3NH_2 + 2nCH_2(O)CH_2 \rightarrow RO(CH_2)_3N((CH_2CH_2O)_nH)_2$	ethoxylated etheramine
$RNH(CH_2)_3NH_2 + 2nCH_2(O)CH_2 \rightarrow RNH(CH_2)_3N(CH_2CH_2O)_nH)_2$	ethoxylated diamine
$RNH_2 + nCH_2(O)CH_2 \rightarrow H(OCH_2CH_2)_nN(R)(CH_2CH_2O)_nH$	ethoxylated amine
$RN(Me)_2 + (H_2O_2) \rightarrow RN^+(Me)_2O^-$	amine oxide
$RN(Me)_2 +$ (MeCl or Me_2SO_4) $\rightarrow RN^+(Me)_3\ X^-$	quaternary amine
$R_3N +$ (benzyl chloride) $\rightarrow R_3N^+Bz\ X^-$	quaternary amine
$RCOOH + NH_2(CH_2)_2NH(CH_2)_2NH_2 \rightarrow 4$	imidazoline
$2RCOOH + (HOCH_2CH_2)_2NCH_3 \rightarrow (RCOOCH_2CH_2)_2NCH_3 + H_2O$	ester amine

amide or amine. Amides are formed by direct reaction of the fatty acid and ammonia at 180–200°C and 0.3–0.7 MPa (3–7 bar), through dehydration of the initially formed salt. Long-chain amides, e.g., erucamide, are the principle industrial products, used as polythene film additives.

Amines are produced from fatty acids in a reaction sequence in which the nitrile is an intermediate. Nitriles are produced by reaction of the fatty acid with ammonia, giving the amide that is dehydrated in situ at 280–360°C in the liquid phase on a zinc oxide, manganese acetate, or alumina catalyst. Lower temperature and longer reaction times are used with unsaturated fatty acids to avoid polymerization. Hydrogenation with nickel or cobalt catalyst reduces the nitrile to amines via the aldimine ($RCH{=}NH$). Depending on the reaction conditions, the aldimine reacts with hydrogen or primary or secondary amines, giving primary, secondary, or tertiary amines, respectively, as the major product. Primary amines are produced at 120–180°C and 2–4 MPa (20–40 bar); higher temperature and lower pressure favors production of secondary and tertiary amines with a symmetrical substitution at the nitrogen. The long-chain composition closely reflects the fatty acid composition of the feedstock, although hydrogenation conditions can be adjusted to hydrogenate the alkyl chains or induce *cis–trans*-isomerism. The more widely used unsymmetrical tertiary amines are produced from primary amines, amides, or alcohols (Table 7). Reactions converting amines to other surface-active derivatives and for the preparation of other nitrogen-containing compounds are shown in Table 7. These have appeared in several reviews (2, 82, 84, 86, 87).



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6.2. Ethoxylation

Long-chain molecules with active hydrogen (alcohols, amines, and amides) react as nucleophiles with ethylene oxide usually with a basic catalyst. The product has a hydroxyl group that can react with further ethylene oxide, leading to polyoxyethylene products with a range of molecular weights. The average number of ethylene oxide molecules added depends on the reaction conditions and can be adjusted to alter the solubility and surfactant properties of the product.

$$\mathrm{ROH + nC_2H_4O \rightarrow RO(C_2H_4O)_nH}$$

Typical reaction conditions are 120–200°C and pressures of 0.2–0.8 MPa (2–8 bar) with potassium hydroxide or sodium alcoholates as catalyst (83). In the reaction with primary amines, both active hydrogens are replaced before further ethylene oxide addition leading to dipolyoxyethylene derivatives. Polyoxyethylenes have a terminal hydroxyl that may be further functionalized under conditions that do not damage the ether linkages, for example, sulfation.

6.3. Sulfation

Sulfate esters of alcohols or polyoxyethylene alcohols are prepared by reaction with sulfur trioxide in continuous falling-film plants, immediately followed by neutralization with sodium hydroxide to give the sodium salt (81).

$$\mathrm{ROH + SO_3 \rightarrow ROSO_3H}$$
$$\mathrm{ROSO_3H + NaOH \rightarrow ROSO_3Na + H_2O}$$

Alcohol sulfates are not stable in acid and are used in alkaline formulations. C_{12}–C_{16} alcohol sulfates have excellent detergency, high foam, and good wetting properties. Alcohol sulfates are fully biodegradable under aerobic and anaerobic conditions and compete in performance with petrochemical-derived linear alkylbenzene sulfonates (LABS).

Mono- and diacylglycerols are starting materials for sulfate ester surfactants that can be prepared directly from triacylglycerols without reduction to the fatty alcohol. Cocomonoacylglycerol sulfates, used in cosmetic formulations, are produced in a solvent-free process (88). Glycerolysis of coconut oil (mole ratio of glycerol to oil of 2:1) gives the raw material for sulfatization, predominantly mono- and diacylglycerols. Membrane filtration is used to desalt the product.

6.4. α-Sulfonates

The methylene adjacent to the carboxyl group is sufficiently activated to react with sulfur trioxide, giving α-sulfonate products. As allylic methylenes are similarly activated, the reaction is usually carried out with saturated starting materials. The complex reaction involves two moles of sulfur trioxide, giving a disulfonate intermediate that reacts with methyl ester to give the α-sulfonate ester, or on treatment with sodium hydroxide the disodium salt (81). α-Sulfonates have low toxicity and are fully biodegradable.

$$\mathrm{RCH_2COOCH_3 + 2SO_3 \rightarrow RCH(SO_3H)COOSO_2OCH_3}$$
$$\mathrm{RCH(SO_3H)COOSO_2OCH_3 + RCH_2COOCH_3 \rightarrow 2RCH(SO_3H)COOCH_3}$$

6.5. Carbohydrate-Based Surfactants

Carbohydrates and related polyols (as well as amino acids) have attracted attention as the hydrophilic component of nonionic surfactants, particularly as a benign alternative to manufacture using ethylene oxide. Sucrose, glucose, and sorbitol (from hydrogenation of glucose) are available in quantity from renewable resources. Although sorbitol esters have been in use for many years, large-scale synthesis of sugar esters remains difficult because of the similar reactivity of all the carbohydrate hydroxyls, leading to many molecular species in the product. Further difficulties are the insolubility and charring of the carbohydrate in the reaction medium. A more controllable reaction is that between long-chain alcohols and glucose, giving alkyl polyglycosides with the fatty alcohol ether linked only to position C-1 on the glucose ring. Further glucose units are also joined through ether links. Both the alcohol and glucose can be produced from renewable resources (oils and fats and starch, respectively), and the reaction can be carried out in a solvent-free system. In commercial production, glucose is suspended in excess alcohol and reacted at 100–120°C with a sulfonic acid catalyst. The product has an average degree of polymerization of 1.2 to 1.7 glucose units per molecule (Figure 14) and is nonirritant and fully biodegradable (88–91). Alkyl polyglycoside production is currently ~100,000 tons per year, which is used in detergent formulations in place of petrochemical-derived products.

6.6. Dimers and Estolides

A number of different dimers and oligomers are produced from fatty acids and alcohols. These are branched-chain compounds with significantly lower melting points than straight chain structures of similar molecular weight. Fully saturated dimers

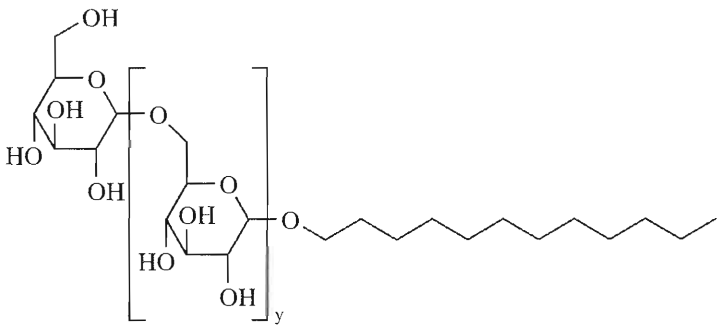


Figure 14. Alkyl polyglycoside. Degree of polymerization $= y + 1$.

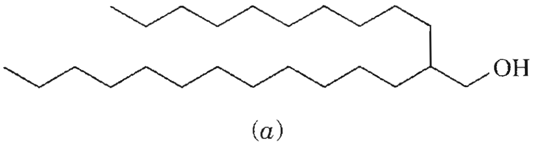
have excellent oxidative stability. This and their extended liquid range are exploited in their use as lubricants and cosmetic additives. Polyfunctional dimers are used in polymer formulations.

Dimer acids. Dimer acids are produced by heating monoene or diene fatty acids (e.g., tall oil acids, a byproduct of wood pulping) with a cationic clay catalyst (92). Typical conditions are 4% montmorillonite at 230°C for 4–8 hours. After distillation, the product is a complex mixture of acyclic, cyclic, and bicyclic dimers along with some trimer. Dimer acids are dibasic and react with diamines and triamines to give polyamides. Imidazole derivatives are used as corrosion inhibitors and esters as lubricants.

Guerbet compounds. Guerbet alcohols have been known for over a century and are produced by the alkali catalyzed dimerization of aliphatic alcohols with accompanying loss of water. Typical reaction conditions are heating at 200–300°C with potassium hydroxide in the presence of transition metal compounds to catalyze the intermediate reduction step. Dehydrogenation of the alcohol to the aldehyde is followed by aldol condensation and rehydrogenation to give the branched-chain alcohol (Figure 15a).

The alcohols can be oxidized to the corresponding acids. Guerbet alcohols, acids, their esters, sulfates, and ether sulfates are used as lubricants, cosmetic additives, and surfactants. Their synthesis, characterization, and applications have been reviewed (93).

Estolides. Estolides are ester-linked branched-chain compounds. They are normally produced under harsh conditions similar to those used to produce dimer acids, but with the addition of around 10% water. Mono- and polyestolides are used as lubricants, greases, and surfactants, and in cosmetic, ink, and plastic formulations. Estolides biodegrade rapidly and completely, at rates comparable with the vegetable oils and fatty acids from which they are derived (94), making them environmentally benign products. The Δ5 monoene acids in meadowfoam oil form estolides under



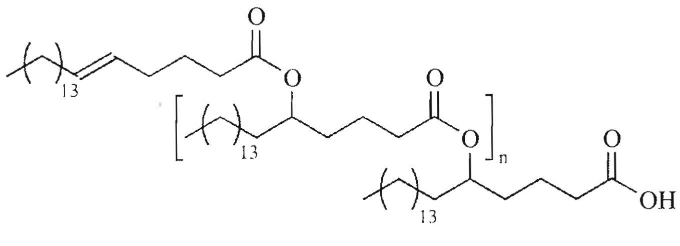


Figure 15. *(a) Guerbet alcohol from lauryl alcohol (12:0). (b) Estolide from meadowfoam acids (20:1 5c).*

mild acid catalysis, neighboring group participation by the carboxyl group facilitating the reaction (Figure 15b) (95). The product from meadowfoam acids shows higher regioselectivity than that from acids with mid-chain olefins where the double bond is further from the carboxyl group. Estolides from mid-chain olefins have significantly lower pour points than the corresponding fatty acids or triacylglycerols, but those from meadowfoam acids show little difference.

7. MODIFYING FATTY ACID STRUCTURE

Isomerization and conjugation change the properties of natural methylene-interrupted fatty acids, leading to new applications and potential added value. Chain shortening or extension produces fatty acids not readily isolated from natural sources and is also used to introduce radioactive or stable isotope labels. Metathesis provides a flexible method for modifying the alkyl chain.

7.1. Isomerization

Trans-isomers of fatty acids are more stable thermodynamically than *cis*-isomers, because of reduced steric crowding; the equilibrium ratio is approximately 4:1 *trans*:*cis*. There is a considerable energy barrier to interconversion (~125 kJ/mole). Before the attached groups can rotate about the double bond, it has to be weakened by coordination to a catalyst, high temperature, or temporary conversion to a single bond through addition and elimination reactions. Chemical isomerization agents leading to an equilibrium mixture include selenium (through a π-complex) and nitrogen oxides or thiols (through free-radical addition/elimination).

Cis-to *trans*-isomerization accompanies partial hydrogenation (see Section 5.2) and may be exploited to raise the melting point. Unwanted isomerization occurs during physical refining at temperatures above 250°C. More unsaturated acids isomerize faster, making linolenic containing seed oils (e.g., soybean and canola) particularly vulnerable. Conditions for deodorizing rape oil without isomerization have been optimized following a detailed study and development of a model of the isomerization kinetics (96).

7.2. Conjugation

Heating with alkali has long been used to produce conjugated drying oils for paints and varnishes. The anion resulting from removal of a bis-allylic methylene rearranges through migration and isomerization, giving a *cis,trans*-conjugated system (Figure 16). Thus, linoleic acid (18:2 9*c*12*c*) gives both 9*c*11*t* and 10*t*12*c* isomers, whereas trienes give a mixture of partially and fully conjugated isomers depending on whether the middle or an outer double bond migrates first. Under the harsh conditions used to prepare drying oils (aqueous alkali at ~230°C), a complex mixture of isomers is eventually formed, but under controlled conditions (e.g., KOH in

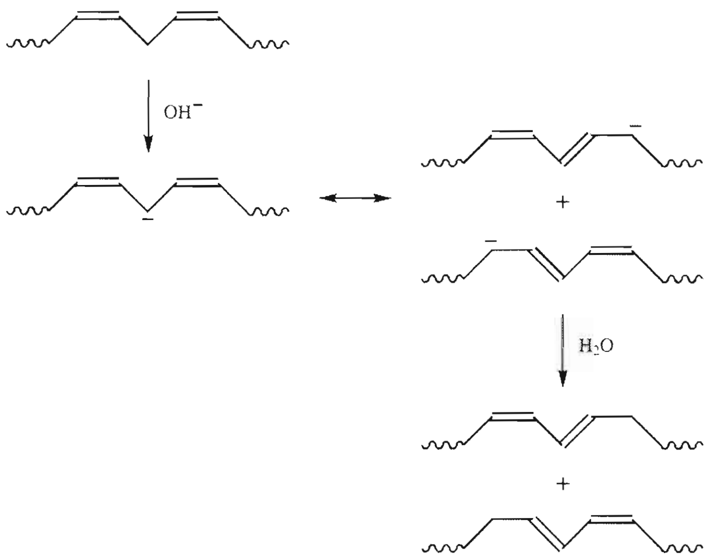


Figure 16. Alkali-induced conjugation of methylene-interrupted olefins.

propylene glycol at 150°C), a mixture containing only the 9*c*11*t* and 10*t*12*c* CLA isomers is produced (97). This product and individual isomers prepared from the mixture are used as nutritional supplements.

Thermal isomerization of linoleic acid produces a conjugated isomer mixture that does not contain all possible *cis*-and *trans*-isomers. The absence of the 8*c*10*t* and 11*t*13*c* isomers suggests a concerted pericyclic mechanism that limits the geometrical possibilities for the rearranged double bonds (98). $[RhCl(C_8H_{14})_2]_2$ in the presence of $(p\text{-}CH_3C_6H_4)_3P$ and $SnCl_2.2H_2O$ is an efficient homogeneous catalyst for the conjugation of linoleic acid, producing conjugated soybean oil with exceptional drying properties and high solvent resistance in high yield (99).

7.3 Chain Shortening and Extension

Fatty acids can be labeled at the carboxyl carbon with ^{13}C or ^{14}C by chain shortening followed by chain extension with labeled carbon. Chain shortening to the norhalide using the Hunsdieker reaction (decarboxylation of fatty acid silver salts in the presence of halogens) is only suitable for saturated acids, but unsaturation is not altered using the alternative developed by Barton employing *N*-hydroxy-pyridine-2-thione in a halocarbon solvent (100). Chain extension with labeled cyanide followed by hydrolysis or reaction of the derived Grignard reagent with labeled carbon dioxide gives the labeled fatty acid. The Barton decarboxylation was recently used to prepare gram quantities of 1-[^{13}C]-linoleic and 1-[^{13}C]-linolenic acids for metabolic studies (101).

Two-carbon chain extension at the carboxyl end, mimicking biosynthesis, uses the malonic ester route (102). After reduction of the carboxyl to an alcohol, the readily displaced mesylate is prepared and reacted with sodium diethylmalonate. Saponification and decarboxylation gives the chain extended product in high yield.

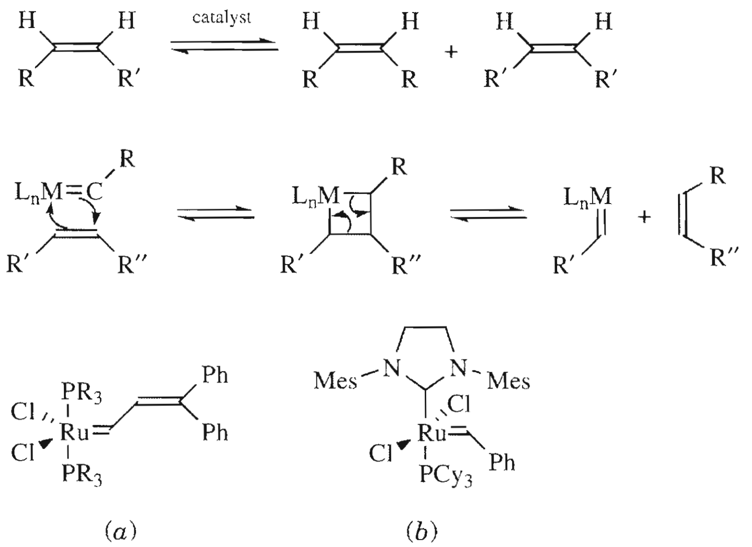


Figure 17. *Olefin metathesis reaction and mechanism. (a) and (b) Grubb catalysts.*

This is an efficient route to C_{20} polyenes, not easily isolated from natural sources, starting from readily available C_{18} sources.

Metathesis (see Section 7.4) provides a flexible route to longer and shorter chains after reaction at a (usually monoene) double bond.

7.4 Olefin Metathesis

Olefin metathesis is the catalytic exchange of groups attached to a double bond. It presents a number of interesting possibilities for modifying the alkyl chain of fatty acids (Figure 17).

The mechanism involves a [2,2] cycloaddition between a transition metal alkylidene complex and the olefin, resulting in an intermediate metallocyclobutane (103). The metallocycle breaks in the opposite way to give a new alkylidene and a new olefin. Repeated exchange at the metal results in an equilibrium mixture of olefins, usually as an equilibrium mixture of *cis*-and *trans*-isomers. The reaction is used in the petrochemical industry to modify hydrocarbon structure, using catalysts such as $WCl_6/SnMe_4$ or Re_2O_7/Al_2O_3. These catalysts are less active when other functional groups compete for the active site, and the application of metathesis in oleochemistry has paralleled development of novel catalysts, such as Grubb catalysts, containing sterically hindered metal alkylidenes (Figure 17a,b).

Self-metathesis describes the reaction of an unsaturated fatty acid with itself. For example, methyl oleate gives a mixture of starting material (50%), unsaturated hydrocarbon (25%), and long-chain unsaturated diester (25%), all as a mixture of *cis*-and *trans*-isomers. (Figure 18). The diester can be converted to the musk component civetone, but a more efficient route is through self metathesis of the ketone oleon derived from methyl oleate by Claisen condensation (104) (Figure 18).

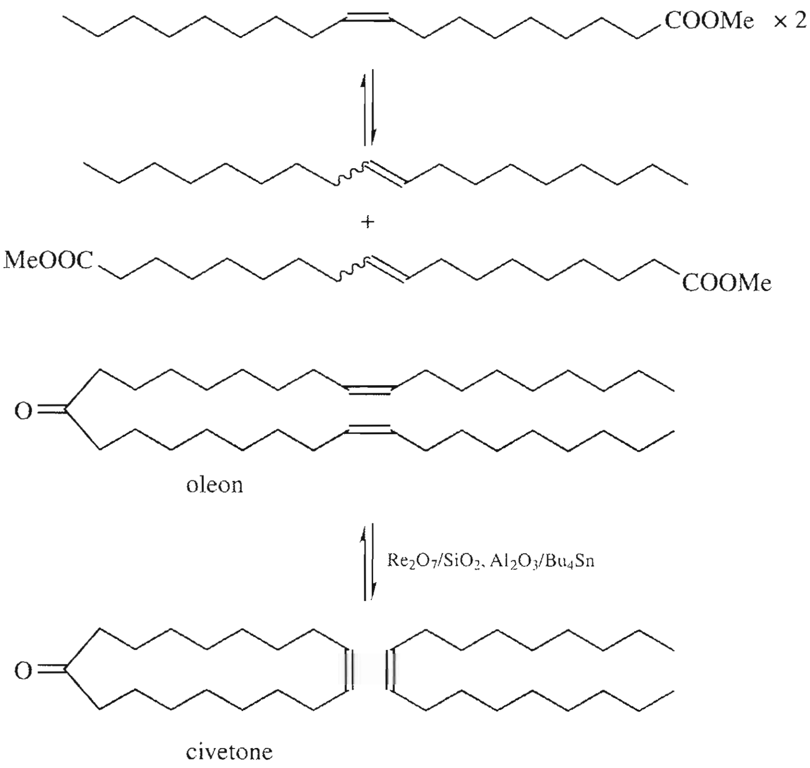


Figure 18. *Self-metathesis reactions.*

Cross-metathesis of an unsaturated fatty ester with a normal alkene is a versatile way of producing chain-shortened or chain-extended homologues leading to oleochemicals with chain lengths outside the C_{16}–C_{22} range of most commodity oils. Methyl oleate reacts with hex-3-ene, in large excess to suppress self-metathesis and push the reaction toward the C_{12} ester and hydrocarbon products. ω-Olefins may be chain extended similarly, the ethene produced being removed to drive the reaction to completion. Cross metathesis provides a route to compounds otherwise difficult to obtain, for example, triacontanol from reduction of the product from methyl erucate and 1-octadecene. Ethenolysis (cross-metathesis with ethene) produces shorter chain ω-olefins with a wide range of applications. A high pressure of ethene is used to force the reaction to the desired products. ω-Olefins produced either by metathesis or from pyrolysis of castor oil can be coupled to give long-chain dibasic acids (105).

Metathesis of intact oils produces polymeric products resulting from intra- and intermolecular bond formation, and they can be used to produce high-viscosity stand oils from drying oils without the loss of double bonds that occurs on thermal polymerization. Vegetable oils can be metathesized efficiently at low temperature and pressure using Grubb's ruthenium catalyst $(Cy_3P)_2Cl_2Ru{=}CHPh$, without the rigorous exclusion of water and oxygen required with $WCl_6/SnMe_4$ (106). Pretreatment of the oil with silica gel may be required.

As a reaction with 100% atom efficiency achieved at moderate temperature (<100°C) using renewable resources, metathesis has potential in a sustainable chemical industry. A recently developed catalyst (Figure 17b) has an efficiency that justifies industrial application in the production of fine chemicals (106). The hydrocarbon byproducts of metathesis, for example, α-olefins, are also valuable starting materials. Metathesis in oleochemistry, in the context of green chemistry, has recently been reviewed (107).

8. NOVEL CHEMISTRY FOR FUNCTIONALIZING THE ALKYL CHAIN

Oils and fats are renewable resources for the chemical industry. Increasing the range of oleochemicals that can be produced could add value to existing crops and provide a market for new crops, driving research into novel fatty acid derivatives. Most current oleochemical production involves reaction at the carboxyl group, with the chain length and unsaturation of the alkyl chain chosen to give the desired melting behavior or hydrophobicity. Introducing functionality to the alkyl chain through radical, electrophilic, nucleophilic, pericyclic, and transition metal catalyzed addition to carbon–carbon double bonds leads to novel compounds with commercial potential. Only a small selection of recent research is illustrated here, focusing on three promising approaches: neighboring group participation, Friedel Crafts acylation, and free-radical addition reactions.

Functionalizing the alkyl chain places more emphasis on the structure of the fatty acids used as feedstock. Model reactions use single fatty acids, often monoenes with particular double-bond positions. Large-scale use of these reactions needs oils rich in single fatty acids to maintain the purity of the product and minimize wasteful side reactions. Suitable feedstocks may be current crops such as high oleic or high erucic varieties or new crops with unusual fatty acids (Chapter xx). Petroselenic acid (18:1 6c) from umbelliferae oils and 5-eicosenoic acid (20:1 5c) from meadowfoam oil are of particular interest as distinctive products can result from neighboring group participation. Breeding to increase the monoene content of some oils may be desirable. ω-Olefins are useful starting materials; 10-undecenoic acid is available from pyrolysis of castor oil, and others may be produced by metathesis (see Section 7.4). Recent, wide-ranging reviews of this area are available (4, 5, 108)

8.1. Neighboring Group Participation

Neighboring group participation is the involvement of a nearby functional group in the reaction of another functional group. It may influence the regioselectivity of the reaction or lead to specific products, often as a result of cyclization to five-and six-membered rings. Neighboring group participation reactions of fatty acids were reviewed recently (109) and can be used to introduce mid-chain functionality, including heterocyclic groups. Double bonds and the carboxyl group usually react independently of each other, but $\Delta 4$ and $\Delta 5$ bonds may interact with the carboxyl through neighboring group participation leading to γ- and δ-lactones (five- and

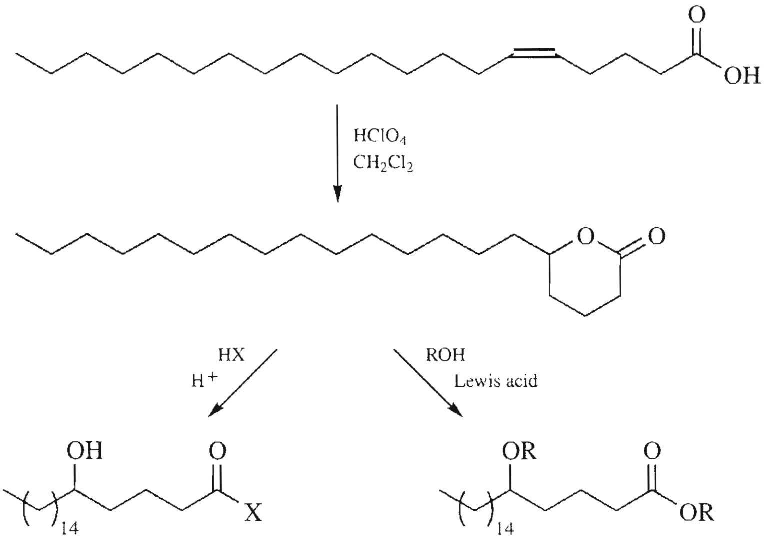


Figure 19. *Neighboring group participation leading to lactones and other products from Δ5 acids. X = OH, RO, or RNH.*

six-membered rings, respectively). The Δ5 acids from meadowfoam oil readily form lactones when refluxed with perchloric acid. The proportion of δ- and γ-lactones depends on the solvent: 6:1 in hexane and 40:1 in dichloromethane. The δ-lactone is formed faster, but the γ-lactone is the more thermodynamically stable isomer. High dilution and a nonparticipating polar solvent that stabilizes the intermediate cation favor kinetic control of the reaction (110). The lactones can be ring opened by treatment with water, alcohols, and amines in acid, giving 4- and 5-hydroxy acids, esters, and amides (111); alternatively, treatment with an alcohol and a Lewis acid catalyst under more vigorous conditions results in an alkyl group ether linked to the chain (112) (Figure 19).

8.2. Friedel Crafts Acylation

Friedel Crafts acylation with an acyl chloride and Lewis acid catalyst is more often associated with aromatic compounds. Ethylaluminium dichloride ($EtAlCl_2$) is an effective catalyst for the acylation of aliphatic olefins, including fatty acids and alcohols, giving β,γ-unsaturated ketones (113). The reaction occurs with both terminal and internal double bonds, with the acyl group becoming attached to one of the double-bond carbons while the double bond migrates one carbon. Reaction at terminal olefins is regiospecific with addition to the terminal carbon giving a linear product and a predominantly *trans*-double bond. Internal double bonds give an approximately equal mixture of *trans*-regioisomers (Figure 19). α,β-Unsaturated acid chlorides give allyl vinyl ketones that undergo Nazarov cyclization to prostaglandin- and jasmonate-like molecules (Figure 20) (114). Neighboring group participation in petroselenic acid (18:1 6*c*) leads to intramolecular cyclization (115). Friedel Crafts acylation is a flexible route to new and highly functionalized oleochemicals containing reactive allyl keto functions (115).

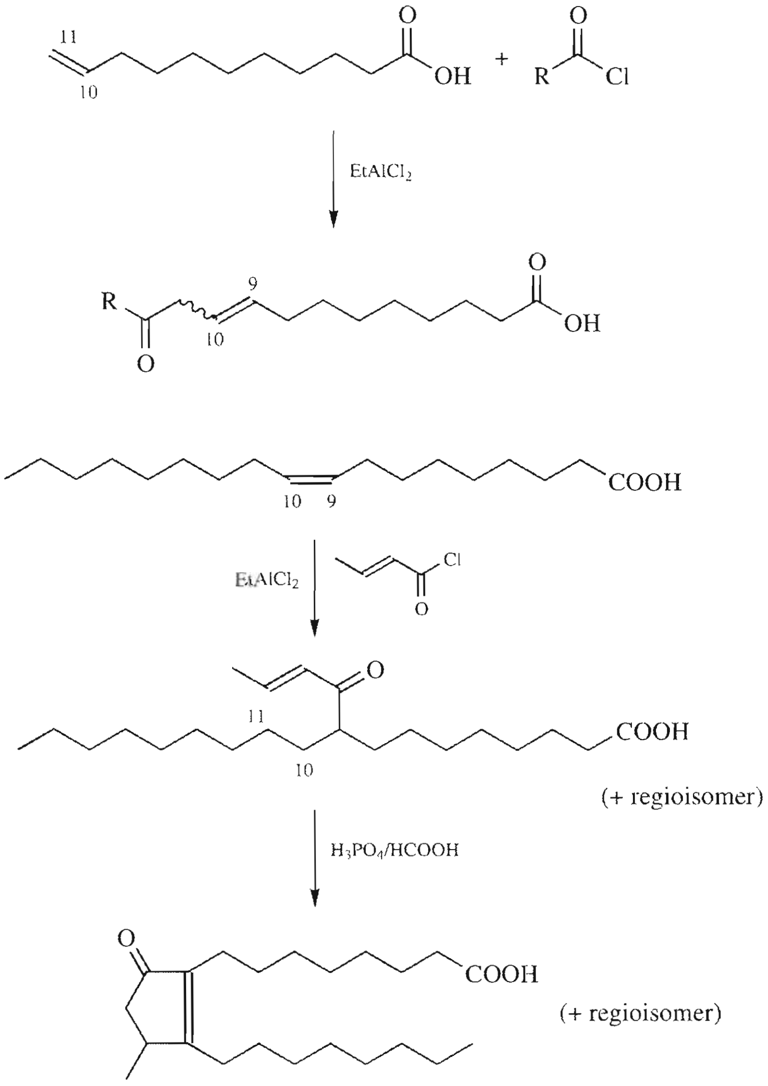


Figure 20. *Friedel Crafts acylation reactions.*

8.3. Free Radical Addition Reactions

Double bonds participate in free radical addition reactions, and these can be of synthetic use in introducing functional groups (116). A particularly simple reaction is the preparation of γ-lactones by solvent-free addition of 2-halocarboxylates to fatty esters, catalyzed by commercial copper powder at 100–130°C (117). Iodides are most reactive and can be prepared in situ from more readily available bromides and sodium iodide (Figure 21).

Perfluoro alkyl iodides add to both terminal and internal double bonds when the reaction is initiated by electron transfer from metals such as finely divided silver, copper powder, and lead with copper acetate. Using an ω-olefin and a perfluoroalkyl-α,ω-diiodide, a perfluoro group can be inserted into a long-chain compound (118) (Figure 21). Deiodination of the product by catalytic reduction results in highly hydrophobic alkyl chains with interesting surfactant properties.

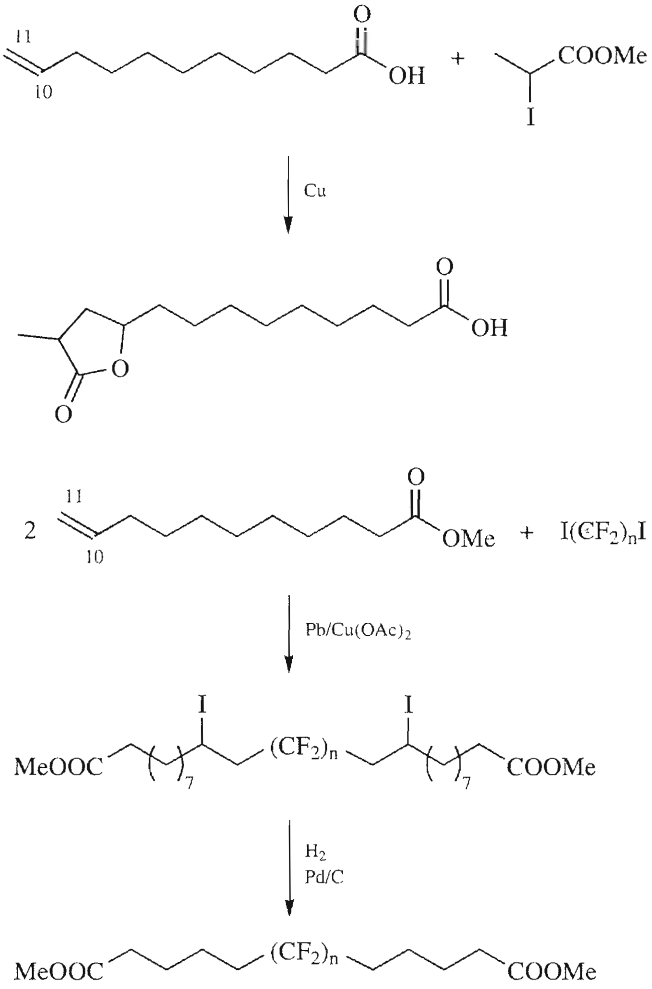


Figure 21. *Radical addition reactions.*

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Attachment 14 section 9

AR 201 - 13055

PINE CHEMICALS ASSOCIATION
P.O. BOX 105113 • ATLANTA, GA 30348-5113 • (770) 446-1290 • FAX (770) 446-1487

DEC 15 2008

May 23, 2001

Administrator
US EPA
P.O. Box 1473
Merrifield, VA 22116

Re: HPV Test Plans and Robust Summaries for Tall Oil and Related Substances and Tall Oil Fatty Acids and Related Substances

Dear Ms Whitman;
On behalf of the member companies of the Pine Chemicals Association's High Production Volume Chemical Task Force, I am pleased to submit the Test Plans and Robust Summaries for the chemical categories designated as:

"Tall Oil and Related Substances"

"Tall Oil Fatty Acids and Related Substances"

The submission includes one electronic copy of each in pdf format, and a hard copy which will be mailed to EPA Headquarters. The registration number for our Consortium is

Should you have any questions concerning our submission please feel free to contact me at (770) 209-7534 or at wjones@tappi.org.

Sincerely,

Walter L. Jones
President & COO

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2001 MAY 31 AM 9:43

MR 48236

AR201- 13056A

HIGH PRODUCTION VOLUME (HPV) CHEMICAL CHALLENGE PROGRAM

TEST PLAN

for

TALL OIL
AND
RELATED SUBSTANCES

CAS No. 8002-26-4
CAS No. 8016-81-7
CAS No. 68140-I 6-9
CAS No. 68152-92-I
CAS No. 65997-01-5
CAS No. 68647-71-2
CAS No. 65997-02-6

Submitted to the US EPA

BY

The Pine Chemicals Association, Inc.
HPV Task Force
Consortium Registration #

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Test Plan For Tall Oil and Related Substances

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Summary

The Pine Chemicals Association, Inc. (PCA) is sponsoring 36 HPV chemicals. This Test Plan addresses the following seven chemicals, known collectively as Tall Oil and Related Substances:

8002-26-4, Tall Oil
8016-81-7, Tall Oil Pitch
68140-16-9, Tall Oil Pitch, sodium salt
68152-92-1, Tall Oil, disproportionated
65997-01-5, Tall Oil, sodium salt
68647-71-2, Tall Oil, potassium salt
65997-02-6, Wastewater, tall oil soap acidulation

These seven substances are all derived from or closely related to tall oil, a by-product from the pulping of pine trees. Tall oil and the various derivatives in this group are all complex mixtures (Class 2 substances). They are composed of numerous chemicals -- the most common of which are rosin and fatty acids, with lesser amounts of terpenes and sterols. Each species of pine tree yields a somewhat different mix of tall oil, and even within a species, the composition of the tall oil could be influenced by the climate and local terrain. However, all the members of this group are similar in chemical composition, being predominantly the extractives that remain after the pulping of wood. Thus, PCA has elected to treat these chemicals as a category for purposes of the HPV program.

Where applicable, PCA will conduct physical/chemical property and environmental fate testing on these substances. Available data show tall oil is non-toxic in acute studies. PCA will conduct testing for the other SIDS health effects endpoints. A representative of the category will be used for ecotoxicity, *in vitro* genotoxicity, and mammalian toxicity testing.

Tall oil is the source of most of the substances in this category, except acidulation wastewater (which is essentially wastewater containing about 1 - 2 % tall oil). Tall oil is used as the feedstock for fractional distillation, from which a variety of useful fractions (rosin, fatty acids, distilled tall oil, heads and pitch) are derived.

Tall oil pitch (the residue after other fractions are distilled away) is primarily consumed as fuel by the tall oil processor; small amounts are converted to salts for use in the asphalt industry. Tall oil salts are used in the production of soaps and detergents, and in metal working fluids. Disproportionated tall oil is used in the rubber industry as a processing aid.

Tall oil (CAS# 8002-26-4) has been selected as the representative substance in this group for testing for the SIDS data. PCA has reviewed existing data on tall oil and determined that other than acute toxicity, there are no other data on the SIDS endpoints. The available data demonstrate that tall oil is non-toxic following acute oral exposure. Because there are no data on ecotoxicity, repeat dose toxicity, *in vitro* genotoxicity, reproductive or developmental toxicity, tall oil will be tested to fulfill these endpoints. A brief summary of the available data for the substances in this category, and the anticipated additional testing, is described below and in Table 1.

Table 1
Matrix of Available Adequate Data and Proposed Testing On Tall Oil and Related Substances*

Chemical and CAS #	Required SIDS Endpoints										
	Partition Coef.	Water Sol.	Biodeg.	Acute Fish	Acute Daph.	Acute Algae	Acute oral	Repeat Dose	In vitro genetox (bact.)	In vitro genetox (non-bact)	Repro/ Develop
8002-26-4, Tall Oil	Test	Test	Adeq.	Test	Test	Test	Adeq.	Test	Test	Test	Test/ Test
8016-81-7, Tall Oil Pitch	Test	LM	Adeq.	C	C	C	C	C	C	C	C
68140-16-9, Tall Oil Pitch, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C
68152-92-1, Tall Oil, dispro-portionated	Test	Test	Test	C	C	C	C	C	C	C	C
65997-01-5, Tall Oil, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C
68647-71-2, Tall Oil, potassium salt	Test	Test	Test	C	C	C	C	C	C	C	C
65997-02-6, Wastewater, tall oil soap acidulation	No test	No test	No test	C	C	C	C	C	C	C	C

Adeq.	Indicates adequate existing data
Test	Indicates proposed testing
No test	See test plan for explanation
LM	Lack of a suitable analytical method precludes testing
C	Indicates category read-down from existing or proposed test data on tall oil.

*No testing will be conducted for melting point, boiling point, vapor pressure, hydrolysis, photodegradation and transport and distribution between environmental compartments, as explained in the test plan.

Physical/Chemical Properties

Physical and chemical properties will be determined when appropriate; however, many of the physical and chemical properties are either inappropriate or cannot be measured for these compounds:

- The melting point will not be determined because these substances will not give a sharp melting point.
- Boiling points cannot be determined because these substances will decompose before they boil.
- Under ambient conditions, the vapor pressure of these chemicals is essentially zero and experimental measurement is not possible.
- The partition coefficients will be tested for six of the substances in this category. Partition coefficient testing can yield a range of values representing the various components, rather than a single value representing the mixture.
- The water solubility of five of the compounds in this grouping category will be determined.

Environmental Fate

With respect to the SIDS environmental fate endpoints:

- Determination of photodegradation is not relevant, since the vapor pressure of these compounds at ambient temperature is essentially zero and they could not enter the atmosphere.
- Hydrolysis in water will not be determined for any of the compounds in this category because the members of this category have low water solubility and lack a functional group that would be susceptible to hydrolysis.
- Biodegradation data will be generated for four of the compounds for which data are not already available.
- Transport and distribution between environmental compartments will not be determined due to the inability to provide usable inputs to the required model.

Ecotoxicity

- Existing ecotoxicity data are not reliable due to inconsistencies in, or artificial methods of, sample preparation. Consequently, tall oil will be retested for acute toxicity to fish, daphnia and algae under conditions that maximize the solubility, but reduce exposure to insoluble fractions that may cause nonspecific toxicological effects.

Mammalian Toxicity

- For the SIDS human health endpoints, there are sufficient data on acute toxicity for tall oil demonstrating that this compound is non-toxic. Data will be generated for tall oil for repeat dose toxicity, reproductive and developmental toxicity using OECD 422, as well as *in vitro* genotoxicity testing.

The Pine Chemicals Association, Inc. HPV Task Force includes the following companies:

Akzo Nobel Resins
Akzo Nobel - Eka Chemicals Incorporated
Arizona Chemical Company
Asphalt Emulsion Manufacturers Association
Boise Cascade Corporation
Cognis Corporation
Eastman Chemical Co. (including the former Hercules Inc. Resins Division)
Georgia-Pacific Resins Inc.
ICI Americas (including the former Uniqema)
Inland Paperboard & Packaging, Inc.
International Paper Co. (including the former Champion International Corporation)
Koch Materials Co.
McConnaughay Technologies, Inc.
Mead Corp.
Packaging Corporation of America
Plasmine Technology, Inc.
Raisio Chemicals
Rayonier
Riverwood International
Smurfit - Stone Container Corporation
Westvaco
Weyerhaeuser Co.

The Task Force will be filing multiple test plans covering various chemicals. Not all members of the Task Force produce the substances covered by this test plan.

I. Description of Tall Oil and Related Substances

The Pine Chemicals Association, Inc. (PCA) is sponsoring seven HPV chemicals known collectively as Tall Oil and Related Substances. This group of chemicals consists of the following:

8002-26-4, Tall Oil
8016-81-7, Tall Oil Pitch
68140-l 6-9, Tall Oil Pitch, sodium salt
68152-92-1, Tall Oil, disproportionated
65997-01-5, Tall Oil, sodium salt
68647-71-2, Tall Oil, potassium salt
65997-02-6, Wastewater, tall oil soap acidulation

This group of chemicals are all closely related to tall oil, which is a by-product from the alkaline pulping of wood, especially pinewood. The precursors of tall oil in the tree are the so-called extractives that make up about 1% of the weight of the wood. These extractives are composed of numerous chemicals, the most common of which are rosin and fatty acids, with lesser amounts of terpenes and sterols. The extractives dissolve in the pulping liquor and are recovered from the liquor when it is concentrated and skimmed. The skimmed material is called tall oil soap and is the sodium salt of tall oil (CAS# 65997-01-5).

Tall oil soap is then acidulated with sulfuric acid to yield crude tall oil (CAS# 8002-26-4). A by-product of this acidulation is "wastewater, tall oil soap acidulation" (CAS# 65997-02-6), which is essentially a solution of sodium sulfate containing dilute amounts of tall oil. Commercially, crude tall oil is fractionally distilled to manufacture tall oil fatty acids and tall oil rosin. These important substances are the key members in other categories of HPV chemicals being sponsored by the Pine Chemicals Association, Inc. An intermediate fraction from the distillation process is distilled tall oil, which has the same CAS registry number as crude tall oil.

The other members of this HPV category are all closely related to tall oil. Disproportionated tall oil (CAS# 68152-92-1) is tall oil that has been stabilized to oxidation. Tall oil pitch (CAS# 8016-81-7) is the residue remaining when the tall oil fatty acids and the tall oil rosin have been distilled away. Its main use is for its fuel value. Zinkel and Russell (1989) noted that use of a material similar to tall oil pitch dates back to biblical times. In Genesis 6:14, Noah was instructed to *"pitch the ark within and without,"* indicating the historical use of pine tree resins, The remaining members of the group are simple salts of either tall oil or pitch.

As complex mixtures, tall oil and its derivatives are all considered Class 2 substances. Information on their composition, uses and the challenges of chemical analysis of these complex mixtures is described below.

A. Composition

All the members of this category are chemically complex, with their composition dependent on the source of the trees from which they were derived and the conditions under which the tall oil was distilled. They are all Class 2 substances. Consequently, they are not described in terms of their chemical composition, but only in general terms such as their acid number or their overall fatty acid or resin acid content (Zinkel and Russell 1989). However, some general information on the typical composition of each of the seven substances in this category is provided below.

1. Tall Oil (CAS# 8002-26-4)

The TSCA Inventory describes tall oil as, *"A complex combination of tall oil rosin and fatty acids derived from acidulation of crude tall oil soap and including that which is further refined. Contains at least 70% rosin."* The two chief types of tall oil covered by this description are crude tall oil and distilled tall oil. The composition of a typical crude tall oil produced in the southeastern U.S. and a typical distilled tall oil are given in Table 2.

Table 2

Composition of Typical Tall Oils

	Crude Tall Oil	Distilled Tall Oil
Acid number	165	185
Fatty acids (%)	52	65
Resin acids (%)	40	30
Unsaponifiable matter (%)	8	5

The actual composition of both types of tall oil can vary widely. The composition of crude tall oil depends on the species of tree from which it was derived, while the composition of distilled tall oil depends upon the species of tree as well as the processing conditions under which it was manufactured. More detailed information on the composition of the tall oil to be tested for the HPV endpoints is provided in Table 3. The structures of some representative resin acids are shown in Figure 1.

Table 3
Comoosition of Distilled Tall Oil To Be Tested

Palmitic acid	$CH_3(CH_2)_{14}COOH$	3%
Palmitoleic acid”	$CH_3(CH_2)_XCH=CH(CH_2)_YCOOH$	1%
Stearic acid	$CH_3(CH_2)_{16}COOH$	1%
Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	28%
Linoleic acid	$CH_3(CH_2)_4CH=CH\text{-}CH_2CH=CH(CH_2)_7COOH$	19%
Linoleic acid, conjugated[b]	$CH_3(CH_2)_XCH=CHCH=CH\text{-}(CH_2)_YCOOH$	9%
Other fatty acids[c]		7%
Isopimaric acid		3%
Abietic acid		10%
Dehydroabietic acid		5%
Other resin acids		11%

a: $x+y=12$
b: x usually 4 or 5; y usually 7 or 8; but $x + y = 12$
c: 5,9,12-octadecatrienoic acid; linolenic acid; 5,11,14-eicosatrenoic acid; cis,cis-5,9-octadecadienoic acid; eicosadienoic acid: elaidic acid; cis-1 1 octadecanoic acid; C-20, C-22, C-24 saturated acids.

2. Tall Oil Pitch (CAS# 8016- 81-7)

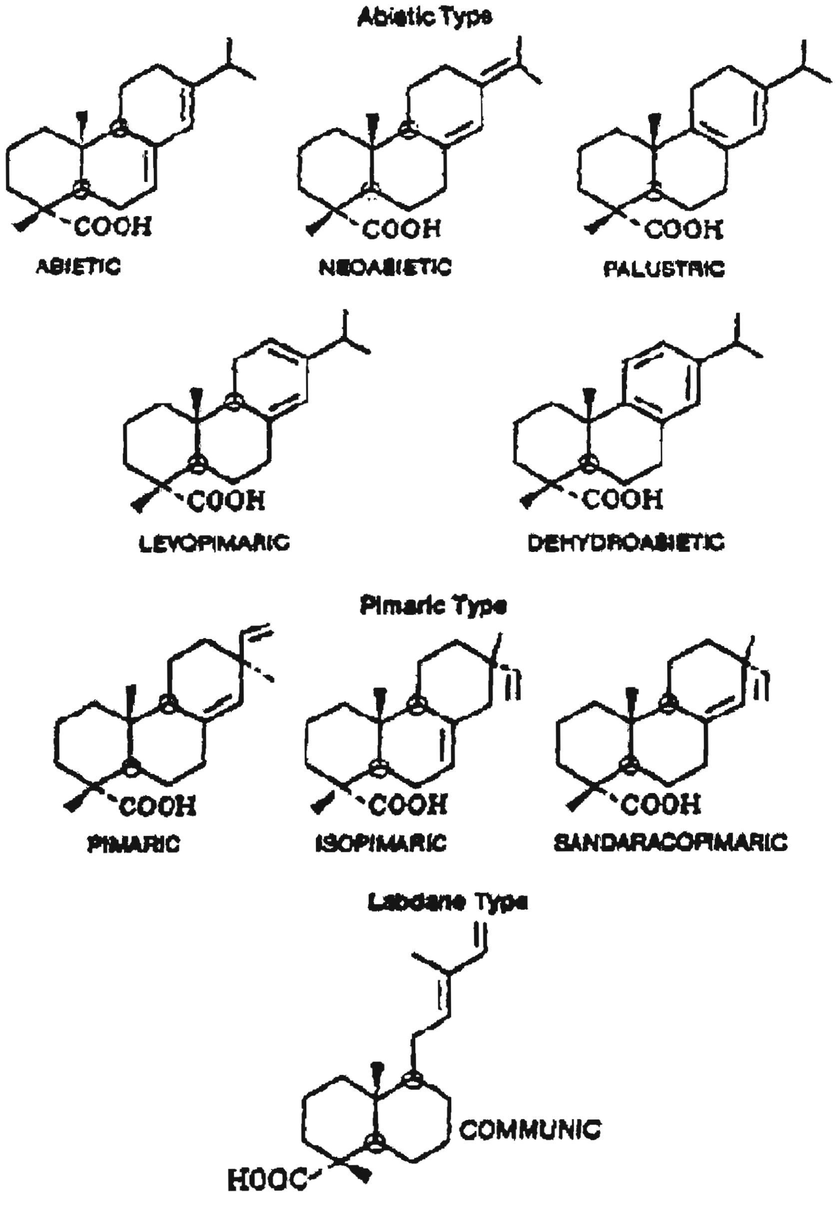
Tall oil pitch is a tarry semi-solid material with a composition very dependent on the processing conditions under which it was produced. As a consequence of its low acid number, its complex composition and its physical form, most of the pitch produced is consumed for its fuel value.

The TSCA Inventory defines tall oil pitch as ***“the residue from the distillation of tall oil. It contains primarily high boiling esters of fatty acids and rosin. It may also contain neutral materials, free fatty acids and resin acids”.*** Pitch is primarily made up of high boiling, high molecular weight compounds formed at the high temperatures encountered during the fractionation process. These compounds include the esters of fatty acids and rosin, and small amounts of dimers and trimers of resin acids and fatty acids. Because pitch has such an extremely complex and variable composition, chemical analysis is not possible, and no typical composition can be presented.

3. Tall Oil Pitch, Sodium Salt (CAS# 68140- 16-9)

This substance is made by neutralizing tall oil pitch with sodium hydroxide. It is sold as an aqueous dispersion.

Figure 1



Common Resin Acids

Figure 1 shows the structures of some representative resin acids found in distilled tall oil and its derivatives.

4. Tall Oil, Disproportionated (CAS# 68152-92-l)

Disproportionated tall oil is distilled tall oil that has been heated with a catalyst that removes conjugated double bonds. The fatty acid and resin acid contents of the treated product are the same as the starting distilled tall oil (see Table 2), but some of the individual components are changed. For example, abietic acid is converted to dehydroabietic acid and linoleic acid is converted to oleic acid.

5. Tall Oil, Sodium Salt (CAS # 65997-01-5) and Potassium Salt (CAS # 68647-71-2)

The sodium salt of crude tall oil is also known as tall oil soap, the precursor to tall oil. Both the sodium and potassium salts of tall oil are also produced from distilled tall oil. The salts are made by treating tall oil with the appropriate base and dispersing the salt formed in water. These compounds, as the salts of a strong base and a weak acid, result in alkaline dispersions with the pH dependent on the salt concentration in the dispersion.

6. Wastewater, Tall Oil Soap Acidulation (CAS # 65997-02-6)

The TSCA Inventory defines this byproduct as, *"The aqueous layer formed by acidulation of tall oil soap with sulfuric acid during the production of tall oil. Composed primarily of a solution of sodium sulfate, the remainder being lignin and tall oil.* " Typically, tall oil soap acidulation wastewater is about a 12% solution of sodium sulfate, containing about 1 to 2% tall oil. This material has no commercial value except as a minor source of sodium for a kraft pulp mill. When that outlet is not available, the wastewater is typically discharged into a mill's wastewater treatment system.

No testing is planned for this material. The Pine Chemicals Association, Inc. (PCA) and the American Forest & Paper Association (AF&PA) petitioned the EPA to remove this byproduct from the HPV list on the grounds that it is an inorganic byproduct and should not be on the list, EPA suggested instead that this material should be treated as "dilute tall oil" since it contains some minor amount of tall oil and did not require independent testing.

B. Commercial Uses of Tall Oil and Related Substances

Tall oil is by far the most important member of this category from a commercial standpoint. The main use of tall oil is as a feedstock to the fractionation process, where tall oil is separated into its various fractions (rosin, fatty acids, distilled tall oil, heads, pitch).

Tall oil pitch, a tarry substance, is mainly consumed as fuel by the tall oil processor.

Tall oil pitch, sodium salt is used in the asphalt industry as a bonding agent in paving applications, or as a plasticizer in asphalt coatings.

Tall oil, disproportionated is important in the copolymerization of styrene and butadiene to produce rubber (SBR) and it is also used in the production of neoprene.

Tall oil, sodium and potassium salts are used in the production of soaps and detergents, as well as in metalworking fluids and lubricants.

Tall oil soap acidulation wastewater is composed of dilute tall oil and is of no commercial value. It is either recycled to the pulping process for the relatively small sodium value or is routed to the producer's wastewater treatment system.

C. Complexity of Analytical Methodology

All of the substances in this category are Class 2 substances. This, combined with the fact that tall oil is essentially insoluble in water and decomposes on heating at high temperature, creates a variety of analytical issues. Gas chromatography of methylated derivatives is the accepted method for the analysis of the members of this category. However, the solubility of tall oil is very low (about 10 ppm). PCA has verified the reliability of the standard analytical methods at such low concentrations. Based on the method validation work to date, it appears that the analytical procedures for tall oil and the remaining substances in this group (with the exception of pitch) will be adequate for the proposed testing. In spite of intensive efforts to develop an analytical method for pitch, analysis has proved to be impossible due to the complexity of this material.

II. Rationale for Selection of Representative Compound for Testing

Tall oil (CAS# 8002-26-4) (which includes crude and distilled tall oil) has been chosen as the representative of this category for testing purposes because it is commercially the most important member of the category. It is the commercial source of most of the substances in this category and the others are associated with its production. In addition, tall oil is the source of almost all of the 36 substances included in the entire PCA HPV program.

All the substances in this category are similar in chemical composition, being predominantly tall oil or its salts. Distilled tall oil will be used as the representative substance in this group for testing for the applicable SIDS ecotoxicity and mammalian toxicity tests. Distilled tall oil is more uniform in composition and physical state than crude tall oil. In addition, products based on distilled tall oil are far more common than those based on crude tall oil, which is used almost exclusively as a distillation feed.

Another criterion listed by EPA for grouping chemicals into a category is the use of the "family approach" of examining related chemicals when they are acids or acid salts, Although the salts of tall oil and tall oil pitch have different physical characteristics, they are included in this group because they are quickly converted into the free tall oil or tall oil pitch when they are treated by acid or by dilution, as they would be under typical toxicity testing conditions.

In summary, this category of chemicals fits the requirements of the EPA's HPV Challenge program for a chemical category, and tall oil is the most appropriate representative test material from this category.

III. Review of Existing Data and Development of Test Plan

PCA has undertaken a comprehensive evaluation of all relevant data on the SIDS endpoints of concern for the chemicals in this category. Other than acute toxicity, there are no other data on the HPV SIDS endpoints for this category. The availability of the data on the specific SIDS endpoints is summarized in Table 4 (identical to Table 1). Table 4 also shows where data will be generated.

Table 4
Matrix of Available Adequate Data and Proposed Testing
On Tall Oil and Related Substances[*]

Chemical and CAS #	Required SIDS Endpoints										
	Partition Coef.	Water Sol.	Biodeg.	Acute Fish	Acute Daph.	Acute Algae	Acute oral	Repeat Dose	In vitro genetox (bact.)	In vitro genetox (non-bact)	Repro/ develop
8002-26-4, Tall Oil	Test	Test	Adeq.	Test	Test	Test	Adeq.	Test	Test	Test	Test/ Test
8016-81-7, Tall Oil Pitch	Test	LM	Adeq.	C	C	C	C	C	C	C	C
68140-16-9, Tall Oil Pitch, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C
68152-92-1, Tall Oil, dispro-portionated	Test	Test	Test	C	C	C	C	C	C	C	C
65997-01-5, Tall Oil, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C
68647-71-2, Tall Oil, potassium salt	Test	Test	Test	C	C	C	C	C	C	C	C
65997-02-6, Wastewater, tall oil soap acidulation	No test	No test	No test	C	C	C	C	C	C	C	C

Adeq. Indicates adequate existing data
Test Indicates proposed testing
No **test** See test plan for explanation
LM Lack of a suitable analytical method precludes testing
C Indicates category read-down from existing or proposed test data on tall oil.

[*] No testing will be conducted for melting point, boiling point, vapor pressure, hydrolysis, photodegradation, and transport and distribution between environmental compartments as explained in the test plan.

A. Evaluation of Existing Physicochemical Data and Proposed Testing

The basic physicochemical data required in the SIDS battery includes melting point, boiling point, vapor pressure, partition coefficient (K_{ow}), and water solubility.

Class 2 substances are composed of a complex mixture of substances and are often difficult to characterize. As noted above, tall oil, tall oil pitch, disproportionated tall oil and their various salts are Class 2 substances. Their composition is variable and cannot be represented by a definite chemical structural diagram. Due to this "complex mixture" characteristic of tall oil and related compounds, some physical property measurements, such as the partition coefficient are of questionable value because the methodology used to determine these properties will actually fractionate or partition the substances into various components. Since the methodology will alter the actual sample composition, the results of these tests are likely to be erroneous, difficult to interpret or meaningless.

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1. Melting Point

Tall oil and the other non-salts in this grouping category are liquids at room temperature; tall oil pitch is a semi-solid. A sharp melting point cannot be obtained for any of these compounds due to the complex nature of these substances. The salts are solids under ambient conditions and heating them to determine the melting point would cause thermal decomposition.

2. Boiling Point

All of the non-salt members of this category are produced by high temperature, high vacuum distillation and are non-volatile at ambient temperatures. A boiling point at ambient pressure has no significance because when heated **to** high temperatures these materials will thermally decompose before they boil. The two salts in this category are solids. When heated to high temperatures, they will also thermally decompose before boiling. Accordingly, measurement of this property is inappropriate for all the substances in this category.

3. Vapor Pressure

Vapor pressures for tall oil and the other chemicals in this category at ambient temperatures are effectively zero, and their experimental measurement is inappropriate. The salt members of the category are solids and thus have no vapor pressure, so this end point cannot be measured. When dissolved in water, their solutions will reflect the vapor pressure of the water rather than the salt, and therefore measurement of this property is inappropriate.

4. Water Solubility

The water solubility of five compounds in this category will be determined using OECD protocol (105). The lack of a suitable analytical method for tall oil pitch precludes the determination of the water solubility.

5. Partition Coefficient

The partition coefficient (i.e., K,,) for six compounds in this category will be determined. Adequate data exist for tall oil and pitch although both will be retested with the other compounds in this category. Because all of these substances are Class 2 mixtures, the procedure (OECD 107) to determine the K_{ow} often yields a number of separate K_{ow} values rather than a single value representative of the mixture. Thus, the results will represent the partition coefficients of the components rather than the mixture.

Summary of Physicochemical Properties Testing: The water solubility of tall oil, disproportionated tall oil and two of the salts will be determined. The partition coefficients for six members of this category will be determined. Adequate data exist for tall oil and pitch although both will be retested with the other compounds in this category. Tests for the melting point, boiling point and vapor pressure are inappropriate.

B. Evaluation of Existing Environmental Fate Data and Proposed Testing

The fate or behavior of a chemical in the environment is determined by the rates or half-lives for the most important transformation (degradation) processes. The basic environmental fate data covered by the HPV Program includes biodegradation, stability in water (hydrolysis as a function of pH), photodegradation and transport and distribution between environmental compartments.

1. Biodegradation

Biodegradability provides a measure for the potential of compounds to be degraded by microorganisms. Depending on the nature of the test material, several standard test methods are available to assess potential biodegradability.

Of the chemicals in this category, two (tall oil and tall oil pitch) have existing data on the biodegradation endpoint. Biodegradation for disproportionated tall oil and the three salts will be determined.

2. Hydrolysis

Hydrolysis as a function of pH is used to assess the stability of a substance in water. Hydrolysis is a reaction in which a water molecule (or hydroxide ion) substitutes for another atom or group of atoms present in an organic molecule. If there is no group suitable to be displaced, then the organic compound is considered to be resistant to hydrolysis. None of the substances in the tall oil category contains an organic functional group that might be susceptible to this physical degradative mechanism. Therefore, hydrolysis need not be measured.

In addition, low water solubility often limits the ability to determine hydrolysis as a function of pH. All of the tall oil compounds have very low solubility in water. Therefore, these materials are expected to be stable in water and it would be unnecessary to attempt to measure the products of hydrolysis. With respect to the various tall oil salts, since they exist in an aqueous medium they hydrolyze (ionize) immediately, but form stable species. Consequently, it would also be unnecessary to measure this endpoint for tall oil salts.

3. Photodegradation

Due to their low water solubility and lack of any vapor pressure at ambient temperatures, there is no opportunity for any of these chemicals to enter the atmosphere. Thus, photodegradation is irrelevant. In addition, based on the constituents in these.complex mixtures, there is no reason to suspect that they would be subject to breakdown by a photodegradative mechanism. Consequently, this endpoint will not be determined for any of the substances in this category.

4. Transport and Distribution Between Environmental Compartments

The transport and distribution between environmental compartments is intended to determine the ability of a chemical to move or partition in the environment. The determination of this property requires the use of various models (e.g., level III model from the Canadian Environment Modeling Centre at Trent University). For Class 2 substances such as tall oil and related compounds, the required inputs to the model are either not available or impossible to determine including molecular mass, reaction half-life estimates for air, water, soil, sediment, aerosols, suspended sediment, and aquatic biota. In addition, while the partition coefficient is also required and can be determined, the multiple K_{ow} values typically derived for these substances (e.g., eight K_{ow} values for tall oil) are a consequence of sample fractionation and reflect various components in the mixture and are not representative of the mixture itself. Consequently, due to the inability to provide usable inputs to the required model, no determination of transportation and distribution between environmental compartments will be undertaken for tall oil and related compounds.

Summary of Environmental Fate Testing: Biodegradation data will be generated for four compounds in this category for which data are not already available. Photodegradation, hydrolysis and transport and distribution between environmental compartments are not applicable to these chemicals.

C. Evaluation of Existing Ecotoxicity Data and Proposed Testing

The basic ecotoxicity data that are part of the HPV Program include acute toxicity to fish, daphnia and algae. While there are existing data on these endpoints for some of the substances in this category, these data are conflicting and it is impossible to determine which, if any, of these findings are representative of ecotoxicity. The inconsistencies in how water samples were prepared for testing these endpoints render these data inadequate. Consequently, acute toxicity to fish, daphnia and alga will be retested for tall oil under conditions that maximize the solubility under the specific test exposure conditions, but reduce exposure to insoluble fractions that may cause nonspecific toxicological effects. In addition, the effect of both filtering to further minimize nonspecific physical effects, and of reducing the pH to the lower end of the acceptable range for test organism survival, will also be investigated for changes in toxicological effects. The results of preliminary tests will be used to select the most appropriate test conditions for the definitive test for each species.

Summary of Ecotoxicity Testing: The acute toxicity of tall oil to fish, daphnia and algae will be tested under conditions that maximize the solubility of the test material, but reduce exposure to insoluble fractions that may cause nonspecific toxicological effects.

D. Evaluation of Existing Human Health Effects Data and Proposed Testing

1. Acute Oral Toxicity

Acute oral toxicity studies investigate the effect(s) of a single exposure to a relatively high dose of a substance. This test is conducted by administering the test material to animals (typically rats or mice) in a single gavage dose. Harmonized EPA testing guidelines (August 1998) set the limit dose for acute oral toxicity studies at 2000 mg/kg body weight. If less than 50 percent mortality is observed at the limit dose, no further testing is needed. A test substance that shows no effects at the limit dose is considered essentially nontoxic. If compound-related mortality is observed, then further testing may be necessary.

Summary of Available Acute Oral Toxicity Data

Tall oil **is** non-toxic following acute oral exposure. The acute oral toxicity of tall oil has been determined in two studies in rats. The acute oral LD_{50} was > 5000 mg/kg in one study and > 6000 mg/kg in another study.

Summary of Acute Oral Toxicity Testing: Tall oil has been tested for acute oral toxicity and found to be non-toxic (i.e., LD_{50} > 5000 mg/kg) well above the guideline of 2000 mg/kg. Consequently, additional testing for this endpoint is not necessary.

2. Repeat Dose Toxicity

Subchronic repeated dose toxicity studies are designed to evaluate the effect(s) of repeated exposure to a chemical over a significant period of the life span of an animal. Typically, the exposure regimen in a subchronic study involves daily exposure (at least 5 consecutive days per week) for a period of not less than 28 days or up to 90 days (i.e., 4 to 13 weeks). The HPV program calls for a repeat dose test of at least 28 days. The dose levels evaluated are lower than the relatively high limit doses used in acute toxicity (i.e., LD_{50}) studies, but still substantially higher than potential human exposure levels. In general, repeat dose studies are designed to assess systemic toxicity, but the study protocol can be modified to incorporate evaluation of potential adverse reproductive and/or developmental effects,

Summary of Available Repeat Dose Toxicity Data

Tall oil will be tested for repeat dose toxicity. The test will be combined with the test for toxicity to reproduction and developmental toxicity in OECD *(422) Combined Repeated Dose Toxicity Study with the Reproduction/Developmental Toxicity Screening Test.*

Summary of Repeat Dose Toxicity Testing: Tall oil will be tested for repeated dose toxicity in conjunction with the reproduction/developmental toxicity screening test (OECD 422).

3. Genotoxicity - In vitro

Genetic testing is conducted to determine the effects of substances on genetic material (i.e., DNA and chromosomes). The gene, which is composed of DNA, is the simplest functional genetic unit. Mutations can occur spontaneously or as a consequence of exposure to chemicals or radiation. Genetic mutations are commonly measured in bacterial and mammalian cells, and the HPV program calls for both types of tests.

Summary of Available Genotoxicity Data

There are no existing data for tall oil for either the bacterial genotoxicity test or the mammalian genotoxicity test. Consequently, tall oil will be tested for both of these endpoints.

Summary of Genotoxicity Testing: Tall oil will be tested for genotoxicity in bacteria (OECD 471) and in vitro in mammalian cells (OECD 473).

4. Reproductive and Developmental Toxicity

Reproductive toxicity includes any adverse effect on fertility and reproduction, including effects on gonadal function, mating behavior, conception, and parturition.

Developmental toxicity is any adverse effect induced during the period of fetal development, including structural abnormalities, altered growth and post-partum development of the offspring.

The “toxicity to reproduction” aspect of the HPV Challenge Program can be met by conducting a reproductive/developmental toxicity screening test or adding a reproductive/developmental toxicity screening test to the repeated dose study (OECD 421 or OECD 422, respectively).

Summary of Reproductive/Developmental Toxicity Data

There are no existing data on tall oil that satisfy this endpoint. Consequently, tall oil will be tested for reproductive/developmental toxicity in conjunction with a repeat dose study using OECD 422.

Summary of Reproductive/Developmental Testing: Tall oil will be tested for reproductive/developmental toxicity in conjunction with a repeat dose study using OECD 422.

References

EPA. 2000. Data Collection and Development on High Production Volume (HPV) Chemicals. Fed. Reg. Dec. 26, Vol. 65(248): pp. 81686-81698.

Zinkel, D.F. and Russell, J., Eds. 1989. Naval Stores. Production, Chemistry, Utilization. Pulp Chemicals Association, New York.

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IV. Robust Summaries of Existing Data

PHYSICO-CHEMICAL PROPERTY – OCTANOL/WATER PARTITION COEFFICIENT	
Test Substance	
Chemical Name	Tall oil
CAS #	8002-26-4
Remarks	This substance is referred to as tall oil in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Testing was conducted according to OECD Test Method 117, "Partition Coefficient (n-Octanol/Water) High Performance Liquid Chromatograph (HPLC) Method"
Test Type	Partition coefficient
GLP (Y/N)	Y
Year (Study Performed)	1993
Test conditions	Tall oil was dissolved in methanol and the solution was analyzed by HPLC with UV detection using a mobile phase of methanol:buffer (3:1) at pH 2 and pH 7.5. As a reference substance, a mixture of seven materials was used.
Results	At pH 2, the log P_{ow} [K_{ow}] values of eight components in tall oil were 6.1, 6.5, 7.0, 7.4, 7.6, 7.8, 8.1, and 8.2. At pH 7.5, the log K_{ow} values of five components in tall oil were 3.5, 4.2, 4.5, 4.7, and 5.4.
Data Quality	Reliable without restrictions – Klimisch Code 1a Note: the various K_{ow} values reflect the components in the mixture and not the mixture *per se*.
References	Dybdahl, H.P. 1993. Determination of log P_{ow} for single components in distilled tall oil. GLP Study No. 408335/475. Water Quality Institute, Hørsholm, Denmark.

PHYSICO-CHEMICAL PROPERTY – OCTANOL/WATER PARTITION COEFFICIENT	
Test Substance	
Chemical Name	Tall oil pitch
CAS #	8016-81-7
Remarks	This substance is referred to as tall oil pitch in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Testing was conducted according to OECD Test Method 117, "Partition Coefficient (n-Octanol/Water) High Performance Liquid Chromatograph (HPLC) Method"
Test Type	Partition coefficient
GLP (Y/N)	Y
Year (Study Performed)	1993
Test conditions	Tall oil pitch was dissolved in methanol and the solution was analyzed by HPLC with UV detection using a mobile phase of methanol:buffer (3:1) at pH 2 and pH 7.5. As a reference substance, a mixture of seven materials was used.
Results	At pH 2, the log P_{ow} [K_{ow}] values of three components in tall oil pitch were 4.3, 6.0, and 6.9. At pH 7.5, the log P_{ow} values of three components in tall oil pitch were 2.8, 3.6, and 4.4.
Data Quality	Reliable without restrictions – Klimisch Code 1a Note: the various K_{ow} values reflect the components in the mixture and not the mixture *per se.*
References	Dybdahl, H.P. 1993. Determination of log P_{ow} for single components in tall oil pitch. GLP Study No. 408335/473. Water Quality Institute, Horsholm, Denmark.

ENVIRONMENTAL FATE – BIODEGRADATION	
Test Substance	
Chemical Name	Tall oil
CAS #	8002-26-4
Remarks	This substance is referred to as tall oil in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Testing was conducted according to OECD Test Method 301 D, "Ready Biodegradability: Closed Bottle Test"
Test Type (aerobic/anaerobic)	Aerobic
GLP (Y/N)	Y
Year (Study Performed)	1993
Contact time	28 days
Inoculum	Secondary effluent from Rungsted Treatment plant
Test conditions	Inoculum: Secondary effluent was collected from Rungsted Treatment plant in Horsholm. Concentration of test chemical: A stock solution of the test material (2 g/L) was prepared in demineralized water by ultra sonication for 5 minutes. After determination of the chemical oxygen demand, the solution was used within the same day. Test Setup: Test medium was prepared by adding 1 mL each of four solutions (potassium phosphate, magnesium sulfate, calcium chloride, ferric chloride) to 1 liter of demineralized water, which was aerated to an initial oxygen concentration of approximately 9 mg O_2/L and inoculated with 1 drop of secondary effluent per liter. The test article was added at 1.96 mg/L to a part of the inoculated test medium, equivalent to a chemical oxygen demand of 5.01 mg O_2/L. Sodium benzoate, the reference compound, was added at 2 mg/L to another part of the inoculated medium (to assess the activity of the inoculum), equivalent to a theoretical oxygen demand of 3.34 mg O_2/L. Both the test and reference articles (1.96 mg/L and 2 mg/L) were added to a third part of the inoculated medium (to assess possible inhibitory effects of the test article), at a theoretical oxygen demand of 8.35 mg O_2/L. Blank controls were prepared using the inoculated medium without test or reference materials. After the samples were prepared, the medium was transferred to calibrated respirometric bottles (BOD bottles), and placed in the dark at 20°C. The study was performed in triplicate. Sampling frequency: Samples were collected for BOD analysis on days 0, 7, 14, 21, and 28.

	Controls: Yes. Method of calculating oxygen demand: Oxygen demand was calculated as the difference between the measured oxygen concentrations at time t and the start of the test. Biological oxygen demand for the added carbon sources was calculated by subtracting the oxygen demand for the blank controls from the oxygen demand in the bottles containing test and reference compounds.
Results	
Degradation % after time	43% after 7 days and 60% after 28 days (test article); 63% after 7 days and 77% after 28 days (sodium benzoate)
Conclusions	The biological oxygen demand for tall oil was 43 and 60% of the theoretical oxygen demand after 7 and 28 days, respectively. These data indicate that the material is dominated by readily biodegradable compounds. Tall oil did not inhibit the respiratory activity of the inoculum. The inoculum had satisfactory activity as demonstrated by more than 60% degradation within the 7 days using the reference compound.
Data Quality	Reliable without restrictions– Klimisch Code 1a
References	Madsen, T. 1993. Biodegradation of distilled tall oil. GLP Study No. 308067/475. Water Quality Institute, Horshplm, Denmark.

ENVIRONMENTAL FATE – BIODEGRADATION	
Test Substance	
Chemical Name	Tall oil
CAS #	8002-26-4
Remarks	This substance is referred to as tall oil in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Testing was conducted according to OECD Test Method 301 F, Manometric respiratory test for biological degradation
Test Type (aerobic/anaerobic)	Aerobic
GLP (Y/N)	Y
Year (Study Performed)	1999
Contact time	28 days
Inoculum	Activated sludge from a municipal sewage treatment plant
Test conditions	Inoculum: Activated sludge from the municipal sewage treatment plant in Reutlingen was washed twice with dechlorinated tap water and centrifuged at 3000 rpm for one minute. Concentration of test chemical: A stock solution of the test material (102.2 mg/L) was prepared. Test Setup: Mineral medium was prepared by adding 10 mL of a potassium phosphate solution and 1 mL each of three other solutions (magnesium sulfate, calcium chloride, ferric chloride) to make a total volume of 1 liter in deionized water. Six flasks were prepared: two of the test article in mineral medium with inoculum (24 mg/L); two of the mineral medium plus the inoculum (24 mg/L); one of the reference substance [sodium benzoate (98.5 mg/L)] with inoculum (24 mg/L); and one of the test article in water with sterilized medium. Sampling frequency: Samples were collected for analysis on days 14 and 28. Controls: Yes. Method of calculating oxygen demand: Biological oxygen demand was calculated by subtracting the oxygen demand for the blank controls from the oxygen demand in the flasks containing test and reference compounds.
Results	
Degradation % after time	73% after 28 days (test article); 97% after 28 days (sodium benzoate)

Conclusions	Seventy-three percent of tall oil was biodegraded after 28 days indicating that the organic portion of the test material was inherently biodegradable.
Data Quality	Reliable without restrictions– Klimisch Code 1a
References	Aniol. S. 1999. Biological degradation, manometric respirometry test. STZ Project No. 04/99. Steinbeis-Transferzentrum Angewandte und Umwelt-Chemie, Reutungen.

ENVIRONMENTAL FATE – BIODEGRADATION	
Test Substance	
Chemical Name	Tall oil pitch
CAS #	8016-81-7
Remarks	This substance is referred to as tall oil pitch in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Testing was conducted according to OECD Test Method 301 D, "Ready Biodegradability: Closed Bottle Test"
Test Type (aerobic/anaerobic)	Aerobic
GLP (Y/N)	Y
Year (Study Performed)	1993
Contact time	28 days
Inoculum	Secondary effluent from Rungsted Treatment plant
Test conditions	Inoculum: Secondary effluent was collected from Rungsted Treatment plant in Horsholm. Concentration of test chemical: A stock solution of the test material (2 g/L) was prepared in demineralized water by ultra sonication for 5 minutes followed by magnetic stirring for 24 hours at 20°C. The solution was filtered and, after determination of the chemical oxygen demand, the solution was used within one day. Test Setup: Test medium was prepared by adding 1 mL each of four solutions (potassium phosphate, magnesium sulfate, calcium chloride, ferric chloride) to 1 liter of demineralized water, which was aerated to an initial oxygen concentration of approximately 9 mg O_2/L and inoculated with 1 drop of secondary effluent per liter. The test article was added at 186 mg/L to a part of the inoculated test medium, equivalent to a chemical oxygen demand of 4.56 mg O_2/L. Sodium benzoate, the reference compound, was added at 2 mg/L to another part of the inoculated medium (to assess the activity of the inoculum), equivalent to a theoretical oxygen demand of 3.34 mg O_2/L. Both the test and reference articles (186 mg/L and 2 mg/L) were added to a third part of the inoculated medium (to assess possible inhibitory effects of the test article), at a theoretical oxygen demand of 7.90 mg O_2/L. Blank controls were prepared using the inoculated medium without test or reference materials. After the samples were prepared, the medium was transferred to calibrated respirometric bottles (BOD bottles), and placed in the dark at 20°C. The study was performed in triplicate. Sampling frequency: Samples were collected for BOD

	analysis on days 0, 7, 14, 21, and 28. Controls: Yes. Method of calculating oxygen demand: Oxygen demand was calculated as the difference between the measured oxygen concentrations at time t and the start of the test. Biological oxygen demand for the added carbon sources was calculated by subtracting the oxygen demand for the blank controls from the oxygen demand in the bottles containing test and reference compounds.
Results Degradation % after time	36% after 7 days and 41% after 28 days (test article); 72% after 7 days and 94% after 28 days (sodium benzoate)
Conclusions	The biological oxygen demand for tall oil pitch was 41% of the theoretical oxygen demand after 7 days and did not increase during the 28 days of the experiment. These data indicate that the material contains readily biodegradable and recalcitrant compounds. Tall oil pitch did not inhibit the respiratory activity of the inoculum. The inoculum had satisfactory activity as demonstrated by more than 70% degradation within the 7 days using the reference compound.
Data Quality	Reliable without restrictions– Klimisch Code 1a
References	Madsen, T. 1993. Biodegradation of tall oil pitch. GLP Study No. 308067/473. Water Quality Institute, Horsholm, Denmark.

ACUTE TOXICITY – ORAL	
Test substance	
Chemical Name	Tall oil
CAS #	8002-26-4
Remarks	This substance is referred to as tall oil in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Test procedure was similar to OECD Test Method 401, "Acute Oral Toxicity"
GLP (Y/N)	N
Year (Study Performed)	1986
Species	Rat
Strain	Sprague-Dawley
Route of administration	Oral
Dose levels	5000 mg/kg
Sex and number/group	5 male and 5 female rats
Frequency of treatment	Single oral gavage
Duration of test	14 day observation post-treatment
Control group (Y/N)	N
Result	
Acute Oral LD_{50}	>5000 mg/kg
Detailed Summary	Crude tall oil (CAS #8002-26-4) was administered orally (via gavage) to Sprague-Dawley rats (n = 5/sex/study) at 5000 mg/kg and the animals were observed for 14 days. The study was performed two times. Parameters evaluated included mortality, clinical signs, body weight gain, and gross pathology. In the first test, one male died on day 1 and a second male died on day 7. For the females, one death occurred on day 1 and a second on day 3. The overall mortality was 40%. No body weight effects were noted. Animals surviving the treatment appeared normal and exhibited no effects at gross pathological examination. In comparison, rats dying on study exhibited erosion of the stomach epithelium and hyperemia of the intestinal tract. When the study was repeated using the same dose level, no deaths occurred, the rats appeared normal throughout, no body weight effects occurred, and there were no gross pathological findings. Based on these data, the oral LD_{50} was greater than 5000 mg/kg.
Data Quality	Valid without restriction – Klimisch Code 1b
Reference	Prince, H.N. 1986. Acute toxicity report: oral toxicity. Report No. GBL 30373. Gibraltar Biological Laboratories, Inc., Fairfield, New Jersey.

ACUTE TOXICITY – ORAL	
Test substance	
Chemical Name	Tall oil
CAS #	8002-26-4
Remarks	This substance is referred to as tall oil in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Test procedure was similar to OECD Test Method 401, "Acute Oral Toxicity"
GLP (Y/N)	N
Year (Study Performed)	1986
Species	Rat
Strain	Sprague-Dawley
Route of administration	Oral
Dose levels	6000 mg/kg
Sex and number/group	5 male and 5 female rats
Frequency of treatment	Single oral gavage
Duration of test	14 day observation post-treatment
Control group (Y/N)	N
Result	
Acute Oral LD_{50}	>6000 mg/kg
Detailed Summary	Crude tall oil (CAS #8002-26-4) was administered orally (via gavage) to Sprague-Dawley rats (n = 5/sex) at 6000 mg/kg and the animals were observed for 14 days. Parameters evaluated included mortality, clinical signs, body weight gain, and gross pathology. One female rat died on day 3; no other deaths occurred. All surviving animals appeared normal throughout the course of the study, and no body weight changes were observed. At gross pathology, no abnormalities were reported in the surviving animals; data for the animal dying on study were not presented. The oral LD_{50} was greater than 6000 mg/kg.
Data Quality	Valid without restriction – Klimisch Code 1b
Reference	Prince, H.N. 1986. Acute toxicity report: oral toxicity. Report No. GBL 30371. Gibraltar Biological Laboratories, Inc., Fairfield, New Jersey.

Attachment 15
section 9

201-14783

HIGH PRODUCTION VOLUME (HPV) CHEMICAL CHALLENGE PROGRAM

FINAL SUBMISSION

for

TALL OIL FATTY ACIDS
AND
RELATED SUBSTANCES

CAS No. 61790-12-3
CAS No. 65997-03-7
CAS No. 68955-98-6
CAS No. 68201-37-6
CAS No. 61790-44-1
CAS No. 61790-45-2

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Submitted to the US EPA

August 2004

By

The Pine Chemicals Association, Inc.
www.pinechemicals.org
HPV Task Force
Consortium Registration

DEC 15 2008

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Final Submission for Tall Oil Fatty Acids and Related Substances

Final Submission for Tall Oil Fatty Acids and Related Substances

Summary

As part of the High Production Volume (HPV) Program, the Pine Chemicals Association, Inc. (PCA) has sponsored 6 HPV chemicals. This final summary addresses the following six chemicals, known collectively as Tall Oil Fatty Acids and Tall Oil Fatty Acid Salts:

61790-12-3, Fatty acids, tall-oil
65997-03-7, Fatty acids, tall-oil, low boiling
68955-98-6, Fatty acids, C16-C18 and C18 unsaturated, branched and linear
68201-37-6, Octadecanoic acid, branched and linear
61790-44-1, Fatty acids, tall oil, potassium salts
61790-45-2, Fatty acids, tall oil, sodium salts

This summary encompasses data previously described in the Test Plan for these substances as well as newly acquired data. The totality of the data shows that these chemicals are all non-toxic.

These substances are all derived from or closely related to tall oil fatty acids, a substance obtained by the fractional distillation of crude tall oil, a by-product from the pulping of pine trees. Tall oil fatty acids and their derivatives are all complex mixtures (Class 2 substances) derived from a natural product. Each species of pine tree has a somewhat different mix of fatty acids, and even within a species, the mix of fatty acids could be influenced by the climate and local terrain.

While these are Class 2 substances, all the members of this group are similar in chemical composition, being predominantly C18 unsaturated and saturated fatty acids, or their salts. Thus, PCA elected to treat the group as a category for purposes of the HPV program. Where applicable, PCA conducted physical/chemical property and environmental fate testing on all six substances. However, a representative of the category was used for ecotoxicity and *in vitro* mammalian toxicity testing. Due to the existence of available data on a representative chemical that satisfied the SIDS human health endpoints, no mammalian testing was necessary.

Tall oil fatty acids (CAS# 61790-12-3) ("TOFA") was selected as the representative substance in this group for testing for the additional SIDS ecotoxicity data. This selection was based upon several factors, including the fact that TOFA represents by far the greatest production volume, with almost four times more TOFA manufactured than all other substances in this group combined. In addition, TOFA is the raw material from which all the other group members, except "fatty acids, tall oil, low boiling," are derived. Consequently, test results obtained on TOFA are most representative of the category.

TOFA and the other members of this group are used primarily as raw materials for the production of other chemicals. For example, the largest use of TOFA is in the production of dimer acids, which are converted into coatings, adhesives and printing inks. TOFA salts are widely used as surfactants in liquid soaps. Other members of the group are used as intermediates in the production of isostearic acid.

The totality of the SIDS data for the substances in this category is briefly summarized below and in Tables 1-3. As shown in these summaries, tall oil fatty acids and related substances are all non-toxic in both mammalian and aquatic test systems. These data are described and discussed in the main document. Detailed Robust Summaries of all relevant data are appended to this document.

Physical/Chemical Properties

The SIDS physical and chemical properties were determined when appropriate; however, many of these endpoints are either inapplicable or cannot be measured for these compounds.

- Melting or boiling points were not determined because these substances will either not give a sharp melting point when heated or will decompose before they melt or boil.
- Under ambient conditions, the vapor pressure of these chemicals is essentially zero and experimental measurement is not possible.
- Water solubility and partition coefficients are summarized in Table 1. It should be noted that although all of the non-salt substances in this category are essentially insoluble in water, considerable effort was undertaken to accurately determine water solubility.
- With respect to the partition coefficient (K_{ow}), the approved method (OECD 117) yields a range of values rather than a single value representative of the mixture. The range of values reflects the partition coefficients of the individual fatty acid constituents of this complex mixture.

The details on these test results are provided in the Robust Summaries.

Table 1. Summary of Physical/Chemical and Environmental Fate Data*

Chemical Name	Required SIDS Endpoint		
	Partition Coefficient	**Water Solubility Mg/l**	**Biodegradation at 28 days**
Fatty acids, tall-oil ("TOFA")	4.9 – 7.6[a]	12.6	56-84%[b]
Fatty acids, tall-oil, low boiling ("heads")	4.4 - 7.8	22.8	41%
Fatty acids, C16-C18 and C18 unsat., branched & linear ("monomer acid")	4.9	15.0	67%
Octadecanoic acid, branched and linear ("hydrogenated monomer acid")	5.6 – 6.1	2.5	46.7%
Fatty acids, tall oil, potassium salts	4.9 – 7.6	Miscible	79%
Fatty acids, tall oil, sodium salts	4.9 – 7.6	Miscible	98.4%

a: A slightly different range was derived from another test; see Robust Summaries for details.

b: These values represent the results from three different tests; see Robust Summaries for details.

*No testing was conducted for melting point, boiling point, vapor pressure, hydrolysis, photodegradation, and transport and distribution between environmental compartments as explained in main document.

Environmental Fate

The SIDS environmental fate endpoints were determined where appropriate; however, many of these endpoints are either inapplicable or cannot be measured for these compounds.

- Photodegradation was not relevant, since the vapor pressure of these compounds is essentially zero and they could not enter the atmosphere.
- Hydrolysis in water was not determined for any of the compounds in this category because all have low water solubility and also lack a functional group that would be susceptible to hydrolysis.
- Transport and distribution between environmental compartments (i.e., fugacity) was not determined due to the inability to provide usable inputs to the required model.
- Biodegradation data are summarized in Table 1 and show that these substances are substantially biodegradable in the environment.

The details on these test results are provided in the Robust Summaries.

Ecotoxicity

TOFA was tested for acute toxicity to fish, daphnia and algae at the maximum measured water solubility. In addition, there are also ecotoxicity data on fatty acids, C16-C18 and C18 unsaturated, branched and linear (i.e., known as monomer acid). These data are summarized in Table 2 and show that none of the compounds in this category are toxic to algae, daphnia or fish. The details of these test results are provided in the Robust Summaries.

Table 2. Summary of Ecotoxicity Data

Chemical Name	**Required SIDS Endpoint**		
	Acute Fish 96 hr NOEL_r	**Acute Daphnia 48 hr NOEL_r**	**Acute Algae 72 hr NOEL_r**
Fatty acids, tall-oil ("TOFA")	1000 mg/l	1000 mg/l	854 mg/l
Fatty acids, tall-oil, low boiling ("heads")	C	C	C
Fatty acids, C16-C18 and C18 unsat., branched & linear ("monomer acid")	1000 mg/l	1000 mg/l	1000 mg/l
Octadecanoic acid, branched and linear ("hydrogenated monomer acid")	C	C	C
Fatty acids, tall oil, potassium salts	C	C	C
Fatty acids, tall oil, sodium salts	C	C	C

C = Indicates category read-down from available data
NOEL_{50} = no observed effect loading rate

Mammalian Toxicity

For the SIDS human health endpoints, there were sufficient data for TOFA on acute and repeat dose toxicity, *in vitro* genotoxicity in *Salmonella* (i.e., Ames test), and reproductive and developmental effects. TOFA was tested *in vitro* for genotoxicity in a mammalian chromosome aberration test (OECD 473) both with and without metabolic activation. In addition, as described below, there are also acute oral toxicity data on both the sodium and calcium salts of monomer acid, mammalian chromosomal aberration data on monomer acid calcium salt and *in vitro* genotoxicity in *Salmonella* for monomer acid sodium salt. The mammalian toxicity data are summarized in Table 3 and demonstrate that TOFA is non-toxic. Based on the category approach, results for the test substance also represent other members of the category. The details of these test results are provided in the Robust Summaries.

Table 3. Summary of Mammalian Toxicity Data

Chemical Name	**Required SIDS Endpoints**				
	Acute Oral	**Repeat Dose**	**Genetox (Bacteria)**	**Genetox (Mammalian cells)**	**Repro/ Develop**
Fatty acids, tall-oil ("TOFA")	LD_{50} > 10000 mg/kg	NOEL = 2500 mg/kg/d	+S9 -S9 Neg. Neg.	+S9 -S9 Clastogenic only at overtly toxic concentrations ± S9	No effects; NOEL = 5000 mg/kg/d
Fatty acids, tall-oil, low boiling ("heads")	C	C	C	C	C
Fatty acids, C16-C18 and C18 unsat., branched & linear ("monomer acid")	C	C	C	C	C
Octadecanoic acid, branched and linear ("hydrogenated monomer acid")	C	C	C	C	C
Fatty acids, tall oil, potassium salts	C	C	C	C	C
Fatty acids, tall oil, sodium salts	C	C	C	C	C
Monomer acid, Na salt (not HPV chemical)	LD_{50} > 2500 mg/kg		+S9 -S9 Neg. Neg.		
Monomer acid, Ca salt (not HPV chemical)	LD_{50} > 2500 mg/kg			+S9 -S9 Neg. Neg.	

C= Indicates category read-down from available data.

Non-HPV substances

Overall Hazard Evaluation and Potential Exposure

For potential human health effects, the totality of the SIDS data demonstrates that TOFA is non-toxic. Because all of the chemicals in this group are derived from or closely related to TOFA, as well as the fact that all members of this group are similar in chemical composition, being predominantly C18 unsaturated and saturated fatty acids, or their salts, based on the category approach, it can be inferred that all of the substances in this group are also non-toxic. In addition, the finding of no acute toxicity or *in vitro* genotoxicity for the sodium and calcium salts of monomer acid is further confirmation that the substances in this category are all non-toxic.

TOFA has no acute oral toxicity (i.e., LD_{50} > 10,000 mg/kg), and repeat dose toxicity data demonstrate a no observed effect level (NOEL) of approximately 2500 mg/kg/day. There was no evidence of reproductive or developmental toxicity in a full two-generation study. The lack of acute oral toxicity (i.e., LD_{50} > 2,500 mg/kg) for the sodium and calcium salts of monomer acid is confirmatory of the lack of acute toxicity of the substances in this category. Genotoxicity test results show no evidence of mutagenicity in *Salmonella* (i.e., Ames test) for either TOFA or monomer acid sodium salt. Chromosomal aberrations in Chinese hamster ovary (CHO) cells were evident only at concentrations of TOFA that were overtly toxic to the cells; monomer acid calcium salt was non-clastogenic in human lymphocytes both in the presence and absence of metabolic activation. Consequently, no adverse health consequences would be associated with any exposures to TOFA or related substances. For potential ecotoxicological effects, the data on TOFA and monomer acid demonstrate that all of the substances in this category are non-toxic to aquatic organisms including fish, daphnia and algae.

With respect to potential exposure to the substances in this category, all are consumed almost entirely as industrial intermediates where they are reacted or further distilled to produce other chemicals. Of the various TOFA distillation and reaction products, it is estimated that greater than 75% are marketed and consumed in non-dispersive commercial applications in the production of dimer acids, polyamide adhesive resins, alkyd resins for paint, polyester lubricants, plasticizers, and metal working fluids. Volatization to air and hence inhalation exposure would be minimal due to the essential lack of a vapor pressure for these substances. Exposure in all of these industrial applications is generally limited to dermal contact during manufacture of the numerous products derived from TOFA and related substances.

The Pine Chemicals Association, Inc. HPV Task Force includes the following companies:

Akzo Nobel Resins
Akzo Nobel - Eka Chemicals Incorporated
Arizona Chemical Company
Asphalt Emulsion Manufacturers Association
Boise Cascade Corporation
Cognis Corporation
Crompton Corporation
Eastman Chemical Co. (including the former Hercules Inc. Resins Division)
Georgia-Pacific Resins Inc.
Hercules Incorporated
ICI Americas (including the former Uniqema)
Inland Paperboard & Packaging, Inc.
International Paper Co. (including the former Champion International Corporation)
Koch Materials Co.
McConnaughay Technologies, Inc.
MeadWestvaco (including the former Mead Corp. and the former Westvaco)
Packaging Corporation of America
Plasmine Technology, Inc.
Raisio Chemicals
Rayonier
Riverwood International
Smurfit – Stone Container Corporation
Weyerhaeuser Co.

The Task Force has filed multiple test plans covering various chemicals. Not all members of the Task Force produce the substances covered by this final submission.

Final Submission for Tall Oil Fatty Acids and Related Substances

I. Description of Tall Oil Fatty Acids and Related Substances

The Pine Chemicals Association, Inc. (PCA) sponsored six HPV chemicals known collectively as Tall Oil Fatty Acids and Tall Oil Fatty Acid Salts. The Test Plan for this group of substances was posted on EPA's HPV website on June 14, 2001, with comments from the Physicians Committee for Responsible Medicine (PCRM) and EPA posted on November 1, 2001 and December 3, 2001, respectively. After reviewing these comments, PCA prepared a response (March 3, 2002) which was subsequently posted on EPA's HPV website.

This group of chemicals consists of the following:

61790-12-3, Fatty acids, tall oil
65997-03-7, Fatty acids, tall oil, low boiling
68955-98-6, Fatty acids, C16 - C18 and C18 unsaturated, branched and linear
68201-37-6, Octadecanoic acid, branched and linear
61790-44-1, Fatty acids, tall oil, potassium salts
61790-45-2, Fatty acids, tall oil, sodium salts

All of the chemicals in this group are derived from or closely related to tall oil fatty acids (TOFA), a substance obtained by the fractional distillation of crude tall oil, a by-product from the pulping of pine trees. All the members of this group are similar in chemical composition, being predominantly C18 unsaturated and saturated fatty acids, or their salts. As complex mixtures derived from a natural product, TOFA and its derivatives are all considered Class 2 substances.

Fatty acids are present in the pine tree as glycerol esters and are saponified to sodium salts during the pulping process. These sodium salts are the major component of tall oil soap that is skimmed from spent pulping liquor and acidulated to form crude tall oil. Crude tall oil is then fractionally distilled at high temperatures under vacuum to yield several fractions, two of which are included in this group: TOFA (CAS# 61790-12-3) and fatty acids, tall oil, low boiling (CAS# 65997-03-7). The remaining members of this group are all derived from TOFA (Zinkel and Russell 1989).

A. Composition

Each species of pine tree has a somewhat different mix of fatty acids. Even within a species, the mix of fatty acids may be influenced by the climate and local terrain. Consequently, product specifications for these substances are not given in terms of chemical components, but in general terms such as acid number and iodine value, which are measures of aggregate chemical reactivity (Zinkel and Russell 1989). Provided below is some general information on the typical compositions of each of the six substances in this category.

1. Fatty Acids, Tall Oil (CAS# 61790-12-3)

The composition of a typical tall oil fatty acid (TOFA) is shown in Table 4.

Table 4

Composition of a Typical Tall Oil Fatty Acid

Common Name	***Chemical Structure***	***Percent Composition***
Palmitic acid	$CH_3(CH_2)_{14}COOH$	1
Stearic acid	$CH_3(CH_2)_{16}COOH$	2
Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	48
Linoleic acid	$CH_3(CH_2)_4CH=CH\text{-}CH_2CH=CH(CH_2)_7COOH$	35
Conjugated linoleic acid[a]	$CH_3(CH_2)_XCH=CHCH=CH\text{-}(CH_2)_YCOOH$	7
Other acids[b]		4
Unsaponifiable matter		2

a: x usually 4 or 5; y usually 7 or 8; but x + y = 12

b: 5,9,12-octadecatrienoic acid; linolenic acid; 5,11,14-eicosatrienoic acid; cis,cis-5,9-octadecadienoic acid; eicosadienoic acid; elaidic acid; cis-11 octadecenoic acid; C-20, C-22, C-24 saturated acids.

2. Fatty Acids, Tall Oil, Low Boiling (CAS# 65997-03-7)

The composition of tall oil, low boiling, better known as “tall oil heads,” is even more complex. As with TOFA, the composition of heads depends on the origin of the tall oil and the fractionation conditions. The TSCA Inventory defines tall oil heads as, *“the low boiling fraction obtained by the distillation of tall oil. Contains fatty acids such as palmitic, stearic, oleic and linoleic as well as neutral materials."* The neutral component is also complex, and contains small amounts of various terpenic hydrocarbons, alcohols, aldehydes, phenolics, lignin-derived materials, and other neutral materials. The composition of a typical tall oil heads is shown in Table 5.

Table 5

Composition of a Typical Tall Oil Heads

Common Name	*Chemical Structure*	*Percent Composition*
Palmitic acid	$CH_3(CH_2)_{14}COOH$	36
Stearic acid	$CH_3(CH_2)_{16}COOH$	1
Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	32
Linoleic acid	$CH_3(CH_2)_4CH=CH\text{-}CH_2CH=CH(CH_2)_7COOH$	23
Other acids[a]		8
Unsaponifiable matter		10

a: These are the same as indicated in Table 2 except the amounts of C20, C22, and C24 will be negligible.

3. Fatty Acids, C16-C18 and C18 Unsaturated, Branched and Linear (CAS# 68955-98-6)

Fatty acids, C16-C18 and C18 unsaturated, branched and linear (CAS# 68955-98-6) is better known as monomer acid. It is a co-product obtained in the production of dimer acid from TOFA. (Dimer acid is sponsored under PCA's Dimers and Trimer Test Plan.) It has some of the characteristics of TOFA, except that it has a much lower level of unsaturation and also contains some branched chains. Monomer acid is a complex mixture of fatty acids; the major components of a typical product are shown in Table 6.

Table 6

Composition of a Typical Monomer Acid

Common Name	*Chemical Structure*	*Percent Composition*
Palmitic acid	$CH_3(CH_2)_{14}COOH$	3
Stearic acid	$CH_3(CH_2)_{16}COOH$	3
Branched C18 acids		28
Oleic acid (cis)	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	12
Elaidic acid (trans)	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	24
Other C18 acids[a]		24
Unsaponifiable matter		1

a: Probably cyclic acids of unknown structure.

4. Octadecanoic Acid, Branched and Linear (CAS# 68201-37-6)

Octadecanoic acid, branched and linear (CAS# 68201-37-6) is also known as hydrogenated monomer acid. It is an intermediate in the conversion of monomer acid into isostearic acid. Its composition is similar to the typical monomer acid shown in Table 6 except that all the acids are saturated.

5. Fatty acids, Tall Oil, Potassium Salt (CAS# 61790-44-1) and Sodium Salt (CAS# 61790-45-2)

Fatty acids, tall oil, potassium salt (CAS# 61790-44-1) and fatty acids, tall oil sodium salt (CAS# 61790-45-2) are simple salts of TOFA. The salts are made by treating TOFA with the appropriate base. As they are salts of a weak acid and a strong base, solutions of these salts are alkaline, with the pH depending on the concentration.

B. Commercial Uses of Tall Oil Fatty Acids and Tall Oil Fatty Acid Salts

Tall oil fatty acids (TOFA) is by far the most important member of this group from a commercial standpoint. The main use of TOFA is as a raw material for the production of a wide variety of other chemicals. TOFA has few, if any, uses in its unmodified form. The largest single use of TOFA is for the production of dimer acids that are then converted into coatings, adhesives, and printing inks. (Dimer acids are addressed in another test plan.) Another important end use for tall oil fatty acids is in the production of alkyd resins that go into paints and printing inks. In all of these applications, TOFA improves the film forming properties and drying characteristics of the products into which it is formulated.

The salts of TOFA are widely used as surfactants. The sodium or potassium salts are used in liquid soaps for both industrial and household cleaning and disinfectant products. They also find uses in metal working fluids and in lubricants.

Tall oil heads are generally consumed for their fuel value. Alternatively, when the fatty acid content is sufficiently high, the heads can be sold for its fatty acid value in some of the same markets that use TOFA.

Monomer acid is used in the production of isostearic acid, a liquid C18 acid. In addition, monomer acid can be used in some of the same applications as TOFA, such as soaps and lubricants.

Octadecanoic acid, branched and linear (hydrogenated monomer) is an intermediate in the production of isostearic acid from monomer acid and does not have any other specific commercial use.

Additional information concerning uses, production and potential exposures to the chemicals in this category are described in greater detail below in the section on *Potential Exposure to Tall Oil Fatty Acids and Related Substances*

C. Complexity of Analytical Methodology

All of the substances in this group are Class 2 substances. This, combined with the fact that fatty acids are essentially insoluble in water and decompose on heating at high temperature, created a variety of analytical challenges. Gas chromatography of methylated derivatives was the method used for the analysis of the members of this category. Because the solubility of the free acids is very low (about 10 ppm), the reliability of this analytical method was verified at such low concentrations.

II. Rationale for Selection of Representative Compound for Testing

TOFA (CAS# 61790-12-3) was selected as the representative substance in this group for testing for the applicable SIDS ecotoxicity and *in vitro* mammalian genotoxicity tests. All the substances in this group are similar in chemical composition, being predominantly C18 unsaturated and saturated fatty acids, or their salts. The selection of TOFA as the representative substance was based on several factors. It has by far the greatest production volume, with almost four times more TOFA manufactured than all other substances in this group combined (i.e., 4, 64, and 28 times greater volume than the low boiling fraction, octadecanoic acid, and fatty acids, C16-18, respectively). EPA guidance suggests that testing the substance produced at the greatest volume as the representative chemical of a category would be appropriate. Clearly, TOFA fits this criterion. In addition, TOFA is the raw material from which all the other group members, except for tall oil heads, are derived.

Another criterion listed by EPA for grouping chemicals into a category is the use of the "family approach" of examining related chemicals when they are acids or acid salts. Although the salts of tall oil fatty acids have quite different physical characteristics, they are included in this group because they are quickly converted into the free acids when they are neutralized by acid or by dilution, as they would be under typical toxicity testing conditions. In summary, this group of chemicals fits the requirements of the EPA's HPV Challenge program for a chemical category, and TOFA is the most appropriate representative test material from this group.

After reviewing the *Test Plan for Tall Oil Fatty Acids and Related Substances*, EPA suggested that PCA form a separate category comprised solely of monomer acid (CAS # 68955-98-6) and octadecanoic acid (CAS # 68201-37-6). The Agency questioned whether the test results for TOFA would be representative of these two members of the category due to the branched and linear nature of these two compounds. After carefully considering these comments, PCA concluded that the category should remain as originally proposed in the test plan. Nonetheless, in light of EPA's comments, the Robust Summaries in this document provide additional data from testing conducted by a PCA member company on monomer acid sodium or calcium salts. Although these chemicals are not HPV chemicals (i.e., not currently on IUR and not assigned CAS Numbers), both of these salts of monomer acid will readily dissociate into monomer acid in aqueous solution; thus, the test results for either of these monomer acid salts should be the functional equivalent of the non-salt (i.e., monomer acid). Likewise, the results should also be representative of octadecanoic acid due to similarity of composition and structure. Octadecanoic acid is simply the hydrogenated form of monomer acid. Moreover, since EPA's HPV Guidelines for grouping chemicals into a category endorses the use of the "family approach" of examining related chemicals when they are acids or acid salts, the use of data on the monomer acid sodium or calcium salts as a surrogate for monomer acid is appropriate. These data are included in the robust summaries.

Finally, EPA also noted that it would be helpful to confirm that the branched and cyclic constituents present in two of the category members arise in the processing of tall oil fatty acids to dimer. Based on our knowledge of the chemistry of the formation of monomer acid, the cyclic structures in monomer are predominantly 1,2-disubstituted six-membered rings that arise from the cyclization of the linoleic and linolenic acids present in TOFA. The formation of cyclic acids in monomer is analogous to the well-documented formation of these same structures in heated vegetable fats such as soybean, linseed, and sunflower oils except that the reaction is acid-catalyzed rather than occurring through a radical mechanism as in the case of heated oils.

III. Summary of Data

At the onset of the HPV program, considerable data were available that satisfied most of the SIDS endpoints for this category. Because there were adequate data for most of the human health SIDS endpoints, no additional testing in mammals was necessary in order to complete the required data for the substances in this category. Table 7 summarizes the results from all of the testing conducted on the substances in this category. Table 7 also illustrates where ecotoxicity data or human health effects data from TOFA, monomer acid, or monomer acid sodium or calcium salts can be generalized to other category members.

Table 7
Summary of Data
Tall Oil Fatty Acids and Related Substances*

Chemical Name and CAS No.	Key SIDS Endpoints										
	Partition Coefficient	Water Sol. Mg/l	Biodeg. @ 28 days	Acute Fish 96 hr. $NOEL_r$	Acute Daph. 48 hr. $NOEL_r$	Acute Algae 72hr. $NOEL_r$	Acute oral	Repeat Dose	Genetox *Salmonella*	Genetox (mammal-ian cells)	Repro/ Develop
Fatty acids, tall-oil 61790-12-3	4.9 – 7.6	12.6	56% 74% 84%	1000 mg/l	1000 mg/l	854 mg/l	LD_{50} > 10,000 mg/kg	NOEL= 2,500 mg/kg/d	Neg. ± S9	Clastogen (± S9) only at overtly toxic conc.	No effects. NOEL> 5,000 mg/kg/d
Fatty acids, tall-oil, low boiling 65997-03-7	4.4 – 7.8	22.8	41%	C	C	C	C	C	C	C	C
Fatty acids, C16-C18 and C18 unsat., branched & linear 68955-98-6	4.9	15.0	67%	1000 mg/l	1000 mg/l	1000 mg/l	C	C	C	C	C
Octadecanoic acid, branched and linear 68201-37-6	5.6 – 6.1	2.5	47%	C	C	C	C	C	C	C	C
Fatty acids, tall oil, potassium salts 61790-44-1	4.9 – 7.6	Miscible	79%	C	C	C	C	C	C	C	C
Fatty acids, tall oil, sodium salts 61790-45-2	4.9 – 7.6	Miscible	98%	C	C	C	C	C	C	C	C
Monomer acid, Sodium salt							LD_{50} > 2,500 mg/kg		Neg. ± S9		
Monomer acid, Calcium salt							LD_{50} > 2,500 mg/kg			Neg. ± S9	

C Indicates category read-down from existing data; * No testing was conducted for melting point, boiling point, vapor pressure, hydrolysis, photodegradation, and transport and distribution between environmental compartments as explained in the summary document.

Monomer acid sodium or calcium salts; not sponsored, non-HPV chemicals; no CAS #'s assigned; testing explained in summary document.

A. Physicochemical Data

The basic physicochemical data required in the SIDS battery includes melting point, boiling point, vapor pressure, partition coefficient (K_{ow}), and water solubility.

Class 2 substances are composed of a complex mixture of substances and are often difficult to characterize. Tall oil fatty acids and their derivatives are Class 2 substances that are derived from natural sources. Their composition is variable and cannot be represented by a definite chemical structural diagram. Due to this "multi-component" characteristic of tall oil fatty acids and their derivatives, some physical property measurements are not appropriate as explained below.

In commenting on the Test Plan for TOFA and related substances, EPA suggested that certain physicochemical properties (i.e., vapor pressure and photodegradation) be measured or estimated for some of the individual components of the complex mixtures that comprise all of the members of this category. PCA disagreed with this suggestion primarily because none of the individual components of these complex mixtures is representative of the mixture itself. Rather, this would provide information on chemicals that were outside of PCA's commitment (i.e., substances with different CAS numbers). However, with respect to this issue, the Soap and Detergent Association has agreed to sponsor chemicals that comprise some of the major constituents of TOFA. Thus, EPA will obtain extensive physicochemical data on some of the components of the complex mixtures in this category.

1. Melting Point

TOFA and the other non-salts in this grouping category are liquids at room temperature. In addition, a sharp melting point cannot be obtained due to the complex nature of these substances. Even though the two salts are solids under ambient conditions, heating them to determine the melting point would cause thermal decomposition. Consequently, the melting point was not determined for any of the substances in this category.

2. Boiling Point

All of the non-salt members of this category are produced by high temperature, high vacuum distillation and are non-volatile at ambient temperatures. A boiling point has no significance because these materials will thermally decompose before they boil, when heated to high temperatures. The two salts in this group are solids. When heated to high temperatures, they will also thermally decompose before boiling. Accordingly, measurement of this property was inappropriate for all the substances in this category.

3. Vapor Pressure

Vapor pressures for the fatty acids at ambient temperatures are effectively zero, and their experimental measurement is inappropriate. The salt members of the group are solids and thus have no vapor pressure, so this end point cannot be measured. When dissolved in water their solutions will reflect the vapor pressure of the water rather than the salt, and therefore measurement of this property is inappropriate.

4. Water Solubility

The water solubility of all six compounds in this category was determined using OECD (105) with the results shown in Table 8.

Table 8

Chemical	Water Solubility (mg/l)
Fatty acids, tall oil	12.6
Fatty acids, tall oil, low boiling	22.8
Fatty acids, C16 - C18 and C18 unsaturated, branched and linear (monomer)	15.0
Octadecanoic acid, branched and linear	2.5
Fatty acids, tall oil, potassium salts	Miscible
Fatty acids, tall oil, sodium salts	Miscible

All of these data are presented in detail in the Robust Summaries.

5. Partition Coefficient

Partition coefficient (i.e., K_{ow}) data were available for TOFA, fatty acids, tall-oil, low boiling, and fatty acids, C16-C18 and C18 unsaturated, branched & linear. Data on K_{ow} were determined for three members of this category - octadecanoic acid, branched and linear; fatty acids, tall oil, potassium salts; and fatty acids, tall oil, sodium salts using OECD (107). Although there were adequate data for TOFA, this substance was retested with the other compounds in this category. Because all of the substances in this category are complex mixtures, the procedure (OECD 117) to determine the K_{ow} yields a range of separate values rather than a single value representative of the mixture reflecting the partition coefficients of the individual fatty acid constituents in this complex mixture. The partition coefficient data are shown in Table 9.

Table 9

Chemical	Partition Coefficient (K_{ow})
Fatty acids, tall oil	4.9 – 7.6
Fatty acids, tall oil, low boiling	4.4 - 7.8
Fatty acids, C16 - C18 and C18 unsaturated, branched and linear (monomer)	4.9
Octadecanoic acid, branched and linear	5.6 – 6.1
Fatty acids, tall oil, potassium salts	4.9 – 7.6
Fatty acids, tall oil, sodium salts	4.9 – 7.6

All of these data are presented in detail in the Robust Summaries.

B. Environmental Fate Data

The fate or behavior of a chemical in the environment is determined by the rates or half-lives for the most important transformation (degradation) processes. The basic environmental fate data covered by the HPV Program includes biodegradation, stability in water (hydrolysis as a function of pH), photodegradation and transport and distribution between environmental compartments.

1. Biodegradation

Biodegradability can help to determine the fate of chemicals in the environment because it provides a measure for the potential of compounds to be degraded by microorganisms. Depending on the nature of the test material, several standard test methods are available to assess potential biodegradability. For the substances in this category OECD method 302B was used for the salts and OECD method 301B was used for the non-salts. Existing and new data were generated using different protocols as noted below.

Of the six chemicals in this category, four (TOFA; tall oil fatty acids, low boiling; fatty acids, C16-C18 and C18 unsaturated, branched and linear; and fatty acids, potassium salts) had existing data on the biodegradation endpoint. Biodegradation for "octadecanoic acid, branched and linear" and "tall oil fatty acids, sodium salts" was determined. The data are summarized below in Table 10.

Table 10

Chemical	Percent Biodegradation	Test Method
Fatty acids, tall oil (Test 1)	56	OECD 301D
Fatty acids, tall oil (Test 2)	84	OECD 301F
Fatty acids, tall oil (Test 3)	74	OPPTS 853.110
Fatty acids, tall oil, low boiling	41	OECD 301D
Fatty acids, C16 - C18 and C18 unsat. branched and linear (monomer)	67	OPPTS 853.110
Octadecanoic acid, branched and linear	47	OECD 301B
Fatty acids, tall oil, potassium salts	79	OPPTS 853.110
Fatty acids, tall oil, sodium salts	98	OECD 302B

All of these data are presented in greater detail in the Robust Summaries.

2. Hydrolysis

Hydrolysis as a function of pH is used to assess the stability of a substance in water. Hydrolysis is a reaction in which a water molecule (or hydroxide ion) substitutes for another atom or group of atoms present in an organic molecule. If there is no group suitable to be displaced, then the organic compound is considered to be resistant to hydrolysis. None of the substances in the tall oil fatty acids category contains an organic functional group that might be susceptible to this physical degradative mechanism. Therefore, hydrolysis was not measured for any of the substances in this category.

In addition, low water solubility often limits the ability to determine hydrolysis as a function of pH. All of the tall oil fatty acids have very low solubility in water. Therefore, these materials are expected to be stable in water and it would be unnecessary to attempt to measure the products of hydrolysis. With respect to the fatty acid salts, since they exist in an aqueous medium they hydrolyze (ionize) immediately, but form stable species. Consequently, it was also unnecessary to measure this endpoint for the fatty acid salts.

3. Photodegradation

Due to their low water solubility and lack of any vapor pressure, there is no opportunity for any of the substances in this category to enter the atmosphere. Thus, photodegradation is irrelevant. In addition, based on the constituents in these complex mixtures, there is no reason to suspect that they would be subject to breakdown by a photodegradative mechanism. Consequently, this endpoint was not be determined for any of the substances in this category.

4. Transport and Distribution between Environmental Compartments

The transport and distribution between environmental compartments (i.e., fugacity) is intended to determine the ability of a chemical to move or partition in the environment. There are various mathematical models for estimating fugacity. One of the most frequently referenced models is the level III model from the Canadian Environment Modeling Centre at Trent University. Even the simplest of these models requires estimates of solubility, vapor pressure and octanol/water partition coefficient to estimate fugacity for a single component. For complex class 2 substances such as TOFA and related substances, estimates of any one of these physical parameters for the various known components would span a range of more that a order of magnitude. When combining three or more parameters of equally variable ranges to derive estimates for different environmental media, the variability in the estimate for any given medium would grow geometrically to more that three or more orders of magnitude. This suggests that any estimates based on arbitrarily selected individual components would be essentially useless for any practical purpose. Add to this the additional fact that there is variability in the chemical composition of these substances (as illustrated in Tables 4, 5 and 6, above) and the possible permutations become unmanageable. Consequently, for complex mixtures such as TOFA and related substances, the mathematical models which rely upon estimates for individual components are of no practical use in predicting environmental fate. Consequently, due to the inability to provide usable inputs to the required model, no determination of transportation and distribution between environmental compartments was undertaken for tall oil fatty acids and related compounds

C. Ecotoxicity Data

The basic ecotoxicity data that are part of the HPV Program include acute toxicity to fish, daphnia and algae. While there were existing data on these endpoints for some of the substances in this category, these data were conflicting and it was difficult to determine which, if any, of these findings is representative of true ecotoxicity. The inconsistencies in how water samples were prepared for testing these endpoints rendered these data inadequate. Consequently, acute toxicity to fish, daphnia and alga was retested for TOFA under the same conditions that were used to measure the limit of water solubility. In addition, these tests were conducted under conditions that were designed to maximize the solubility under the specific test exposure conditions, but reduce exposure to insoluble fractions, which may cause nonspecific toxicological effects. In addition, the effect of both filtering, to further minimize nonspecific physical effects, and of reducing the pH to the lower end of the acceptable range for test organism survival, was also investigated for changes in toxicological effects. The results of preliminary tests were used to select the most appropriate test conditions for the definitive test for each species.

In reviewing the *Test Plan for TOFA and Related Substances*, EPA agreed with the proposed acute toxicity testing of fish, daphnia, and algae, but also suggested that PCA conduct a 21-day chronic daphnid reproduction test using a flow-through method with measured concentrations. A 21-day test using a flow-through method would be impracticable, based on the amount of water that would be required due to the substances' extremely low solubility and the difficulty in performing the necessary serial analytical measurements. In addition, where there is a risk of emulsions forming inherently (as there is likely to be with these substances), flow through testing in not possible and is not recommended in OECD (2000) Guidance Document 23 (Aquatic Toxicity Testing of Difficult Substances and Mixtures). As noted above, the methodology for preparing the water for ecotoxicity testing was identical to that used to determine the solubility of TOFA. This procedure was adopted in order to ensure that ecotoxicity testing was conducted at the limit of actual water solubility.

Finally, both EPA and OECD guidance recommend the use of 21-day testing only if the substances have the potential for long-term effects in the aquatic environment, i.e., are bioaccumulative -- which these substances are not. The high K_{ow} values for the components of TOFA (i.e., individual fatty acids) reflect the fact that they are lipid-like materials and not that they bioaccumulate. Thus, chronic aquatic toxicity testing in daphnia should not be necessary for the HPV Program.

It should also be noted that in accordance with EPA's suggestion that the data on TOFA might not be representative of fatty acids, C16 - C18 and C18 unsaturated, branched and linear (i.e., monomer acid) or octadecanoic acid, branched and linear, included in the robust summaries are ecotoxicity data (i.e., fish, daphnia and algae) for monomer acid as well as recently developed ecotoxicity data (i.e., fish and daphnia) on monomer acid, calcium salt. The ecotoxicity data are summarized below in Table 11 and demonstrate that both TOFA and monomer acid are non-toxic to fish, daphnia and algae.

Table 11

Chemical	**Fish** **96 hr. *NOEL$_r$**	**Daphnia** **48 hr. NOEL$_r$**	**Algae** **72 hr. NOEL$_r$**
Fatty acids, tall oil	1000 mg/l	1000 mg/l	500 mg/l
Monomer acid[a]	1000 mg/l	1000 mg/l	1000 mg/l
Monomer acid, calcium salt[b]	100 mg/l	100 mg/l	

*NOEL$_r$ = No Observed Effect Loading Rate
a = For monomer acid all effects were reported as no observed effect concentration loading rates (LOEC$_r$)
b= Highest loading rate tested

These data are presented in greater detail in the Robust Summaries.

D. Human Health Effects Data

1. Acute Oral Toxicity

Acute oral toxicity studies investigate the effect(s) of a single exposure to a relatively high dose of a substance. This test is conducted by administering the test material to animals (typically rats or mice) in a single gavage dose. Harmonized EPA testing guidelines (August 1998) set the limit dose for acute oral toxicity studies at 2000 mg/kg body weight. If less than 50 percent mortality is observed at the limit dose, no further testing is needed. A test substance that shows no effects at the limit dose is considered nontoxic. If compound-related mortality is observed, then further testing may be necessary.

Summary of Acute Oral Toxicity Data

TOFA is non-toxic following acute oral exposure. TOFA was tested for acute oral toxicity in Sprague-Dawley rats. Animals received a single oral (gavage) dose of 10,000 mg/kg and were observed for 14 days. Parameters evaluated included clinical signs, mortality, body weight, and gross pathology. None of the animals died. One hour post-dosing, piloerection was observed in one male and abnormal stance was observed in one male and one female. By four hours, these effects had resolved. No body weight effects were observed. Gross necropsy revealed no treatment-related effects. The acute oral LD_{50} was >10,000 mg/kg. Similarly, both the sodium and calcium salts of monomer acid are non-toxic following acute oral exposure with the oral LD_{50}'s for both > 2500 mg/kg. These data are presented in greater detail in the Robust Summaries.

2. Repeat Dose Toxicity

Subchronic repeated dose toxicity studies are designed to evaluate the effect of repeated exposure to a chemical over a significant period of the life span of an animal. Typically, the exposure regimen in a subchronic study involves daily exposure (at least 5 consecutive days per week) for a period of not less than 28 days or up to 90 days (i.e., 4 to 13 weeks). The HPV program calls for a repeat dose test of at least 28 days. The dose levels evaluated are lower than the relatively high limit doses used in acute toxicity (i.e., LD_{50}) studies. In general, repeat dose studies are designed to assess systemic toxicity, but the study protocol can be modified to incorporate evaluation of potential adverse reproductive and/or developmental effects.

Summary of Repeat Dose Toxicity Data

There are substantial data that demonstrate a lack of toxicity for TOFA. Tall oil fatty acid (CAS #61790-12-3) was tested in a 90-day subchronic toxicity study in rats. The test material was administered to Charles River rats in the diet at concentrations 0, 5, 10, or 25% for 90 days. The approximate doses were 0, 2500, 5000, or 12,500 mg/kg/day. Parameters evaluated included clinical signs, mortality, body weight, body weight gain, food consumption, hematology, clinical chemistry, urinalysis, gross pathology, organ weights, and microscopic pathology.

There were no deaths attributable to the test compound and no clinical signs were observed. Body weight and body weight gain were not affected by treatment, but food consumption was slightly decreased at dietary levels of 10 and 25%. No changes in hematology, clinical chemistry or urinalysis parameters were measured at any dose level. At gross pathology, no treatment-related effects were noted. No consistent organ weight changes and no histopathological effects were reported. Based on these data, the No Observed Effect Level (NOEL) was 5% (approximately 2500 mg/kg/day). Other subchronic studies for 28 and 40 days confirm the low toxicity of TOFA. In these studies, the only effect noted was depression of body weight gain at the highest doses tested. These data are presented in greater detail in the Robust Summaries.

3. Genotoxicity – In vitro

Genetic testing is conducted to determine the effects of substances on genetic material (i.e., DNA and chromosomes). Genetic mutations are commonly measured in bacterial and mammalian cells, and the HPV program calls for completing both types of tests. The genotoxicity data are summarized below in Table 12 and show that TOFA and monomer acid, sodium salt are negative in the Ames *Salmonella* test, monomer acid, calcium is non-clastogenic in mammalian cells while TOFA was clastogenic only at concentrations that were overtly toxic to the cells.

Table 12

Chemical	Ames *Salmonella*		Chromosomal Aberration	
	+S9	-S9	+S9	-S9
TOFA	Neg.	Neg.	Clastogenic (at overtly toxic concentration)	Clastogenic (at overtly toxic concentration)
Monomer acid Sodium salt	Neg.	Neg.		
Monomer acid Calcium salt			Non-clastogenic	Non-clastogenic

These data are presented in greater detail in the Robust Summaries.

4. Reproductive and Developmental Toxicity

Reproductive toxicity includes any adverse effect on fertility and reproduction, including effects on gonadal function, mating behavior, conception, and parturition. Developmental toxicity is any adverse effect induced during the period of fetal development, including structural abnormalities, altered growth and post-partum development of the offspring.

Summary of Reproductive/Developmental Toxicity Data

TOFA had no effects when tested for reproductive and developmental toxicity in Sprague-Dawley rats in a full two-generation study. The test compound was administered in the diet at concentrations of 0, 5 or 10% to 30 females/group and 15 males/group. The approximate doses were 0, 2500, or 5000 mg/kg/day. Males and females in the first generation (F_0) began treatment at 80 days of age and were mated at 100 days of age. Treatment of the F_0 animals continued through the weaning of the first generation (F_1). After weaning, the F_1 males and females were maintained on the treatment diet. At 100 days of age, they were mated and allowed to deliver pups (F_2).

There were no treatment-related effects on reproductive performance, or on any parameter measured in either the F_1 or F_2 pups. No treatment-related changes in fertility, viability, lactation, or gestation indices were observed. Hematology, clinical chemistry and urinalysis parameters were similarly unchanged, and there were no developmental effects in any F_1 or F_2 offspring. TOFA did not alter or otherwise affect the reproduction or development of rats in this study at doses as high as 10% (approximately 5000 mg/kg/day). These data are presented in greater detail in the Robust Summaries.

IV. Category Justification: Validation of Tall Oil Fatty Acids as Representative of Other Category Members for SIDS Endpoints

All of the substances in this group are similar in chemical composition, being predominantly C18 unsaturated and saturated fatty acids, or their salts. In addition, except for tall oil heads, TOFA is the raw material from which all the other group members are derived. However, even for tall oil heads, the composition is qualitatively similar to other members in this category. For TOFA (including sodium and potassium salts) and tall oil heads the primary difference in their respective composition is in the ratios of palmitic, stearic, oleic, linoleic acid, other C18 acids and unsaponifiable matter. On the other hand, monomer acid contains branched and linear constituents including unsaturated oleic acid (cis) and elaidic acid (trans) which are both substantially saturated in hydrogenated monomer. Because the totality of the toxicity data for TOFA demonstrates that it is non-toxic, it is reasonable to infer that the TOFA salts and tall oil heads are similarly non-toxic. While it is also reasonable to conclude that monomer acid and hydrogenated monomer (octadecanoic acid) are similarly non-toxic, additional data add further to this likelihood.

Acute toxicity and *in vitro* mutagenicity data on monomer acid sodium or calcium salts were also available. It is well known that both of these salts of monomer acid will readily dissociate into monomer acid in aqueous solution. Thus, the finding of no acute toxicity or *in vitro* mutagenicity for either salt test is the functional equivalent of the non-salt (i.e., monomer acid). These results are also representative of octadecanoic acid due to similarity of composition and structure since octadecanoic acid is simply the hydrogenated form of monomer acid. In addition, acute ecotoxicity data were also available for monomer acid and monomer acid, calcium salt which demonstrate that neither substance was acutely toxic to fish, daphnia or algae. In summary, based on adequate toxicity data and a detailed understanding of the composition of the six substances in this category, the toxicological data on TOFA (augmented by data on monomer acid and monomer acid salts) can be reliably extrapolated to the entire category thereby validating the composition of the category.

V. Hazard Characterization of Tall Oil Fatty Acids and Related Substances

For potential human health effects, the totality of the SIDS data demonstrates that TOFA is non-toxic. Because all of the chemicals in this group are derived from or closely related to TOFA, as well as the fact that all members of this group are similar in chemical composition, being predominantly C18 unsaturated and saturated fatty acids, or their salts, based on the category approach, it can be inferred that all of the substances in this group are also non-toxic. In addition, the finding of no acute toxicity or *in vitro* genotoxicity for the sodium and calcium salts of monomer acid is further confirmation that the substances in this category are all non-toxic.

TOFA has no acute oral toxicity (i.e., LD_{50} > 10,000 mg/kg), and repeat dose toxicity data demonstrate a no observed effect level (NOEL) of approximately 2500 mg/kg/day. There was no evidence of reproductive or developmental toxicity in a full two-generation study. The lack of acute oral toxicity (i.e., $LD_{50} > 2,500$ mg/kg) for the sodium and calcium salts of monomer acid is confirmatory of the lack of acute toxicity of the substances in this category. Genotoxicity test results show no evidence of mutagenicity in *Salmonella* (i.e., Ames test) for either TOFA or monomer acid sodium salt. Chromosomal aberrations in Chinese hamster ovary (CHO) cells were evident only at concentrations of TOFA that were overtly toxic to the cells while monomer acid calcium salt was non-clastogenic in human lymphocytes both in the presence and absence of metabolic activation. Consequently, no adverse health consequences would be associated with any anticipated exposures to TOFA or related substances.

With respect to potential ecotoxicological effects, the totality of SIDS data on TOFA, the representative substance in this category, as well as for monomer acid, and monomer acid, calcium salt demonstrate that the substances in this category are non-toxic to aquatic organisms including fish, daphnia and algae. The No Observed Effect Loading Rate ($NOEL_r$) for TOFA to both fish and daphnia was 1000 mg/l while the $NOEL_r$ for algae was 500 mg/l. For monomer acid, the no observed effect concentration loading rate ($NOEC_r$) was 1000 mg/l in fish, daphnia and algae. Finally, for monomer acid, calcium salt the $NOEL_r$ for both fish and daphnia was 100 mg/l (i.e., the highest loading rate tested).

VI. Potential Exposure to Tall Oil Fatty Acids and Related Substances

This brief summary provides an overview of market end uses and potential exposure to products derived from Tall Oil, a major feed stock to the pine chemicals industry with emphasis on tall oil fatty acids and related substances. This information along with hazard data developed as part of the High Production Volume Chemical Testing Program should be useful in evaluating the potential risks (if any) that might be associated with various uses of tall oil derived chemicals.

During the process of pulping coniferous trees to make paper, sodium salts of chemicals occurring naturally in the trees are produced as a co-product. When acidulated, this soap becomes Tall Oil. Typically, Tall Oil is a mixture of 25–35% rosin acids and 45–55% fatty acids with the balance being neutral compounds. Tall oil can be further processed or separated into its major components by a process of high temperature low pressure distillation. The recovery and distillation of tall oil began on a commercial scale in the mid twentieth century. As the pulp and paper industry has expanded globally so has the processing of tall oil, and the production of tall oil derivatives. At the present time there are 10 companies operating a total of 19 tall oil distillation plants in 10 countries. The total production of tall oil is approximately two billion pounds per year.

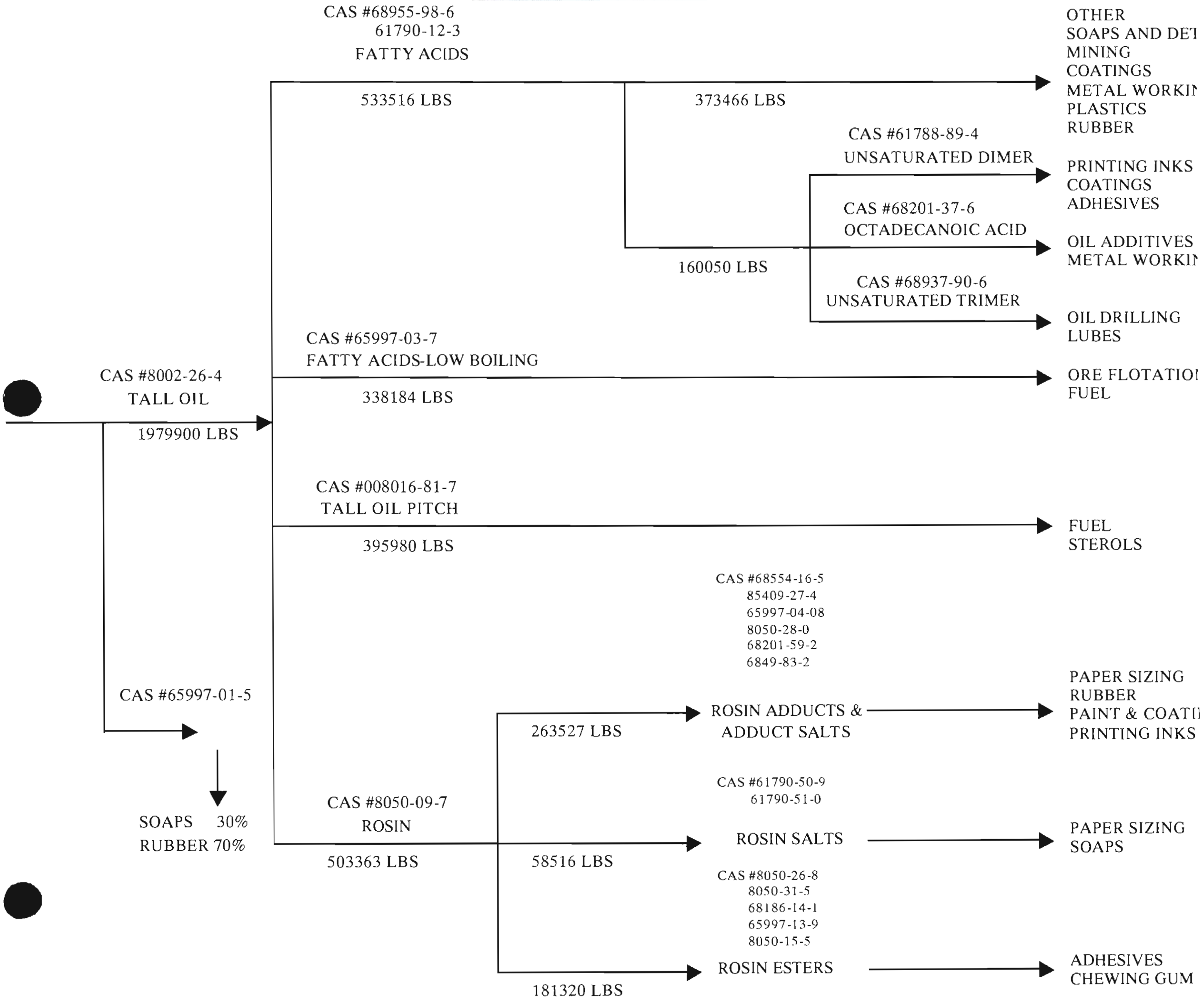
Human exposure is limited by the fact that most tall oil chemicals are industrial intermediates consumed in the production of other chemicals As such there is little, if any, potential for exposure of the general consumer population. Environmental exposure is limited by the fact that the chemical processes used in the tall oil industry are essentially closed system processes where temperature and pressure are carefully controlled.

Environmental releases from tall oil processing plants are limited to (1) treated waste water discharge, and (2) ambient emissions following treatment with scrubbers or thermal oxidizers. Waste water can be generated from operation of the plant pressure control system or from minor spills and leaks associated with the process and/or handling of chemical products and routine housekeeping activities. In all cases the waste water is collected, the stream is treated to remove any free oil, and is then discharged into a lager biological waste treatment facility (either municipal treatment system or the treatment system of the parent company's paper mill). Air emissions generated from the pressure control system or from the storage and transfer of various streams, are generally collected and treated in chemical scrubbers or thermal oxidizers.

The entire array of tall oil based chemicals and their related processing steps are best depicted by a "family tree" or flow diagram rather than a listing of discrete independent chemicals. Such a diagram demonstrates how various "parent" chemicals are consumed in the production of down stream chemicals. Figure 1 is a representation of the "family tree" for tall oil products and the relationship between

U.S. TALL OIL INDUSTRY

PRODUCTION & MARKET DISTRIBUTION
POUNDS/YEAR (000)



these products. Based on industry data approximately 95% of tall oil is consumed during the production of other downstream products.

Two primary fractions (rosin, fatty acids) are derived form the initial processing of tall oil. As can be seen from Figure 1 these primary fractions are further processed to a wide variety of intermediates. Tall oil "Heads," tall oil "Pitch" and distilled tall oil (DTO) are the remaining fractions derived from the processing of tall oil. Each of these fractions or intermediates and their end uses are described in the appropriate Post-testing Final Summary documents for each category of substances.

Tall Oil Fatty Acids & Salts

Tall oil fatty acids (TOFA) are consumed almost entirely as an industrial intermediate where they are reacted or further distilled to produce other chemicals. Table 13 illustrates general use categories and potential exposures to TOFA and related substances. Of the various TOFA distillation and reaction products, it is estimated that greater than 75% are marketed and consumed in non-dispersive commercial applications in the production of dimer acids, polyamide adhesive resins, alkyd resins for paint, polyester lubricants, plasticizers, and metal working fluids. Volatization to air and hence inhalation exposure would be minimal due to the essential lack of a vapor pressure for these substances. Exposure in all of these industrial applications is generally limited to dermal contact during manufacture of the numerous products derived from TOFA and related substances.

Approximately 12% of TOFA production is marketed into the soap and detergent industry. In this application TOFA is reacted to form salts which are constituents in these consumer products. In addition, a small percentage of TOFA production is further processed into oleic and linoleic acids which are cleared for use as direct food additives by the US FDA. The only other potential exposure to any of the substances in this category occurs during their production from activities such as changing reaction vessels, sampling for quality control, transferring material from one work area to another, loading and unloading bulk containers, changing filters, and cleaning equipment.

Table 13

Distribution, Application and Potential Occupational Exposure to Fatty Acids and Related Substances

Substance	CAS #	Primary Function	Use Category	Major End Use Application	%
Fatty Acids, Tall Oil	61790-12-3	Chemical intermediate (feed for fatty acid derivatives)	Site limited/ Industrial	Salts	31
				Mining	17
				Paints & coatings	11
Fatty Acid, C-16,-C18 and C18 unsaturated, branched and linear (monomer acid)*	68955-98-6			Plastics	7
				Dimer	30
				Other	4
Fatty Acids, Low Boiling	65997-03-7	Chemical intermediate	Industrial	Mining	90
				Fuel	10
Octadecanoic Acid, Branched & Linear	68201-37-6	Chemical intermediate (feed for iso-stearic acid)	Site limited/ industrial	Oil additives	85
				Metal working	15
Fatty acids, tall oil, potassium salt	61790-44-1	Chemical intermediate (surfactants)	Site limited/ industrial	Soaps	61
				Metal working fluids	29
Fatty acids, tall oil, sodium salt	61790-45-2			Lubricants	10

*Addressed in Final Submission for Fatty Acid Dimers and Trimer

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EPA. 2000. Data Collection and Development on High Production Volume (HPV) Chemicals. Fed. Reg. Dec. 26, Vol. 65(248): pp. 81686-81698.

Zinkel, D.F. and Russell, J., Eds. 1989. Naval Stores. Production, Chemistry, Utilization. Pulp Chemicals Association, New York.

August 2004

Section 10 List of Attachments

No Attachments.

Section 11 List of Attachments

Attachment 1, section 11: Anna Hyvonen et. al., Tall oil/water –emulsions as water repellents for Scots pine sapwood, Holz als Roh-und Werkstoff (2006) 64: 68-73.

Section 11, attachment 1

Holz als Roh- und Werkstoff (2006) 64: 68–73
DOI 10.1007/s00107-005-0040-5

ORIGINALARBEITEN · ORIGINALS

Anna Hyvönen · Petteri Piltonen · Jouko Niinimäki

Tall oil/water – emulsions as water repellents for Scots pine sapwood

Abstract Like classic wood preservatives, many water repellents have the drawback of being detrimental to the environment. Hence interest in environment-friendly, even biodegradable, substances has increased. Natural oils (e.g. tall oil, linseed oil) appear to be capable of preventing water uptake by wood. However, in order to achieve total sapwood penetration, the amount of oil needed is high. The aim of this study was to investigate the water repellent efficiency of crude tall oil and crude tall oil water emulsions (oil-in-water and water-in-oil emulsions), and the possibilities of reducing the amount of oil needed with the emulsion technique. Scots pine sapwood samples were impregnated with tall oil formulations. The levels of water absorption and the degree of water repellent efficiency were determined with cyclical wetting and drying tests. The results showed that tall oil treatments reduce the water uptake of pine sapwood. With tall oil emulsion treatments almost equal water repellent efficiencies were reached as with pure tall oil, even when the oil retentions were considerably lower. The total amount of oil required could be halved. The emulsion technique is a potential method of decreasing the amount of oil needed in order to protect wood from water uptake.

Tallöl/Wasser-Emulsionen als Hydrophobierungsmittel für Kiefernsplintholz

Zusammenfassung Wie viele klassische Holzschutzmittel haben auch viele Hydrophobierungsmittel den Nachteil, dass sie umweltschädlich sind. Deshalb ist das Interesse an umweltfreundlichen, insbesondere biologisch abbaubaren, Mitteln gestiegen. Natürliche Öle (wie z.B. Tallöl, Leinöl) haben grundsätzlich eine hydrophobierende Wirkung. Um jedoch eine vollständige Imprägnierung des Splintholzes zu erreichen, ist eine große Ölmenge erforderlich. Ziel dieser Arbeit war es, die hydrophobierende Wirkung von Tallöl sowie von Tallöl-Wasseremulsionen (Öl-in-Wasser- und Wasser-in-Öl-Emulsionen) zu untersuchen sowie festzustellen, in welchem Umfang die benötigte Ölmenge durch das Emulgieren reduziert werden kann. Kiefernsplintholzproben wurden mit Tallölgemischen imprägniert. Der Grad der Wasseraufnahme und der Hydrophobierungsgrad wurden mittels zyklischer Befeuchtungs- und Trocknungsversuche bestimmt. Die Ergebnisse zeigten, dass eine Behandlung mit Tallöl die Wasseraufnahme von Kiefernsplintholz reduziert. Behandlungen mit Tallölemulsionen erbrachten annähernd die gleiche Wasser abweisende Wirkung wie solche mit reinem Tallöl, obwohl dabei die eingebrachte Ölmenge deutlich niedriger war. Die erforderliche Ölmenge konnte auf die Hälfte reduziert werden. Die Emulsionstechnik ist eine potenzielle Methode um die Ölmenge, die zum Feuchteschutz von Holz benötigt wird, zu reduzieren.

1 Introduction

Wood can be protected from moisture variations with water repellents, which reduce the rate of liquid water uptake in the capillaries. The rate of water uptake can be considerably reduced either by providing a water barrier, or by rendering the wood hydrophobic; although very few materials are truly hydrophobic with a water/solid contact angle of more than 90° (Borgin and Corbett 1970a). Depending on the amounts used, water repellents applied to wood fill in the cell lumina or are deposited on the external and to some extent on the internal pore surfaces, and impart hydrophobic properties to the surface. Hence, the water cannot spontaneously penetrate the wood pores through capillary action and the rate of water absorption is thus limited (Banks and Voulgaridis 1980). However, without wood modification it is not possible to make the cell wall inert to water Given time, wood treated with water repellent and exposed to water will swell to the same extent as untreated wood. Although water repellents do not stop all water absorption, they are excellent treatment for wood used outdoors, because they inhibit the absorption of liquid water during rain, yet allow the wood to dry after rain (Anonymous 1999a). The reduction in average moisture content and in the period of time when the wood is wet enough to allow attack by micro-organisms slows down the rate of fungal attack (Feist and Mraz 1978, Stamm 1964).

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Tall oil/water – emulsions as water repellents for Scots pine sapwood

Tallöl/Wasser-Emulsionen als Hydrophobierungsmittel für Kiefernsplintholz

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Publisher	Springer Berlin / Heidelberg
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Subject Collection	Biomedical and Life Sciences
SpringerLink Date	Friday, November 11, 2005

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2. Ulvcrona, Thomas (2007) Possibilities for compositional tailoring of Norway spruce (Picea abies L. Karst.) wood using a hydrophobic oil impregnation process . *Holz als Roh- und Werkstoff* 65(2) [CrossRef]
3. Hyvönen, Anna (2006) Using the emulsion technique and an iron catalyst to enhance the wood protection properties of tall oil. *Holz als Roh- und Werkstoff* [CrossRef]

Section 12 List of Attachments

Attachment 1 , section 12: National Organic Standards Board (NOSB), Crops Committee, List 4 Inerts in Pesticide Formulations , Discussion Document, November 2008.

Attachment 2 , section 12: Pesticide EU-MRLs Database , Regulation (EC) No. 396/ 2005.

Attachment 3 , section 12; New Rules on pesticide residues in food, European Commission.

National Organic Standards Board (NOSB)
Crops Committee
List 4 Inerts in Pesticide Formulations
Discussion Document
November 2008

Background:

The National Organic Program (NOP) regulations currently allow the use inert ingredients in pesticide formulations that were previously classified by the EPA
As List 4A- *Minimal Risk Inert Ingredients* and List 4B- *Other ingredients for which EPA has sufficient information to reasonably conclude that the current use pattern in pesticide products will not adversely affect the public health or the environment.*
In accordance with the Food Quality Protection Act, in 2006 the EPA completed reassessments of inert ingredients used in pesticide products to ensure that such products
met human health-based safety standards. Subsequent to that time, the EPA officially notified the NOP that the Inerts List system (Lists 3 and 4) referenced in the NOP regulations in §205.601 and 205.603 is now considered obsolete and no longer in effect.

The NOP needs to amend it's regulations to be in alignment with the modifications the EPA has made to it's regulations. In the meantime, the EPA has agreed to allow the NOP to continue the List 4 designation of allowed materials (as referenced in the August 2004 EPA List 4) while the NOP determines the best way to amend the regulations. The EPA reassessments have removed some materials from their list of minimal risk ingredients (List 4B), which are now prohibited under the NOP. The potential exists for the EPA to add new materials to their list of minimal risk ingredients as well. The EPA minimal risk ingredients can be found in 40 CFR 180.950 – *Tolerance exemptions for minimal risk active and inert ingredients* (attached at the end of this document). As the originator and maintainer of the National List of Allowed and Prohibited Substances in organic production and handling, the NOSB needs to work in concert with the NOP and EPA to accomplish the task of amending NOP inert ingredient regulations as they pertain to the National List.

Current Regulatory Language

§205.601….
m) As synthetic inert ingredients as classified by the Environmental Protection Agency (EPA), for use with nonsynthetic substances or synthetic substances listed in this section and used as an active pesticide ingredient in accordance with any limitations on the use of such substances.
(1) EPA List 4—Inerts of Minimal Concern.
(2) EPA List 3—Inerts of Unknown Toxicity allowed:
(i) Glycerine Oleate (Glycerol monooleate) (CAS #s 37220–82–9)—for use only until December 31, 2006.
(ii) Inerts used in passive pheromone dispensers.
(n) Seed preparations. Hydrogen chloride (CAS # 7647–01–0)—for delinting cotton seed for planting.

§205.603….
(e) As synthetic inert ingredients as classified by the Environmental Protection Agency (EPA), for use with nonsynthetic substances or synthetic substances listed in this section and used as an active pesticide ingredient in accordance with any limitations on the use of such substances.
(1) EPA List 4—Inerts of Minimal Concern.

Plan of Action:

The NOSB will begin public discussion of these matters at their November 2008 meeting. Public comment is invited to comment on the possible solutions described below. **Public comment is heavily encouraged to identify the number and nature of synthetic materials deemed to be vital in pesticide formulations used in organic farming.**

Possible solution options:

1)The NOP has suggested that a substitution of the language in the rule currently as List 4 with the new regulatory reference for 40 CFR 180.950 the minimal risk ingredients (significant correlation to List 4A).

2)Adopt the original 2004 List 4A inerts (Attachment 1) as an itemized list, with ongoing re-assessment through the sunset process.

3) Adopt the minimal risk ingredients currently in 40 CFR 180.950 (significant correlation to List 4A). This would entail a one time adoption of materials currently on this list with ongoing re-assessment through the sunset process.

4) Eliminate blanket inerts lists and adopt a policy of requiring inerts in pesticides to be petitioned individually.

5) Inerts (List 3) currently used in passive pheromone dispensers would be petitioned individually and be subject to regular sunset re-evaluations.

Upon taking the subject under advisement, a final NOSB recommendation could potentially be presented at the Spring 2009 meeting. Considering that the NOSB recommendation will need to be vetted through the EPA, a posting for public comment and NOSB adoption might be more realistically accomplished at the Fall 2009 meeting. Simultaneous to the NOSB review, an Advanced Notice of Proposed Rulemaking (ANPR) would be an important step prior to whichever meeting timetable is selected. Following the vote by the NOSB on a final recommendation on inert ingredients to be included on the National List, proposed rulemaking should proceed.

§ 180.950 Tolerance exemptions for minimal risk active and inert ingredients.

Unless specifically excluded, residues resulting from the use of the following substances as either an inert or an active ingredient in a pesticide chemical formulation, including antimicrobial pesticide chemicals, are exempted from the requirement of a tolerance under FFDCA section 408, if such use is in accordance with good agricultural or manufacturing practices.

(a) *Commonly consumed food commodities.* Commonly consumed food commodities means foods that are commonly consumed for their nutrient properties. The term commonly consumed food commodities shall only apply to food commodities (whether a raw agricultural commodity or a processed commodity) in the form the commodity is sold or distributed to the public for consumption.

(1) Included within the term commonly consumed food commodities are:

(i) Sugars such as sucrose, lactose, dextrose and fructose, and invert sugar and syrup.

(ii) Spices such as cinnamon, cloves, and red pepper.

(iii) Herbs such as basil, anise, or fenugreek.

(2) Excluded from the term commonly consumed food commodities are:

(i) Any food commodity that is adulterated under 21 U.S.C. 342.

(ii) Both the raw and processed forms of peanuts, tree nuts, milk, soybeans, eggs, fish, crustacea, and wheat.

(iii) Alcoholic beverages.

(iv) Dietary supplements.

(b) *Animal feed items.* Animal feed items means meat meal and all items derived from field crops that are fed to livestock excluding both the raw and processed forms of peanuts, tree nuts, milk, soybeans, eggs, fish, crustacea, and wheat. Meat meal is an animal feed composed of dried animal fat and protein that has been sterilized. Other than meat meal, the term animal feed item does not extend to any item designed to be fed to animals that contains, to any extent, components of animals. Included within the term animal feed items are:

(1) The hulls and shells of the commodities specified in paragraph (a)(2)(ii) of this section, and cocoa bean.

(2) Bird feed such as canary seed.

(3) Any feed component of a medicated feed meeting the definition of an animal feed item.

(c) *Edible fats and oils.* Edible fats and oils means all edible (food or feed) fats and oils, derived from either plants or animals, whether or not commonly consumed, including products derived from hydrogenating (food or feed) oils, or liquefying (food or feed) fats.

(1) Included within the term edible fats and oils are oils (such as soybean oil) that are derived from the commodities specified in paragraph (a)(2)(ii) of this section when such oils are highly refined via a solvent extraction procedure.

(2) Excluded from the term edible fats and oils are plant oils used in the pesticide chemical formulation specifically to impart their characteristic fragrance and/or flavoring.

(d) [Reserved]

(e) *Specific chemical substances.* Residues resulting from the use of the following substances as either an inert or an active ingredient in a pesticide chemical formulation, including antimicrobial pesticide chemicals, are exempted from the requirement of a tolerance under FFDCA section 408, if such use is in accordance with good agricultural or manufacturing practices.

Chemical	***CAS No.***
Acetic acid, sodium salt	*127–09–3*
Alpha-cyclodextrin	10016–20–3
Amylopectin, acid-hydrolyzed, 1-octenylbutanedioate	113894–85–2
Amylopectin, hydrogen 1-octadecenylbutanedioate	125109–81–1
Animal glue	None
Ascorbic acid (vitamin C)	50–81–7
Beeswax	8012–89–3
Benzoic acid, sodium salt	532–32–1
Beta-cyclodextrin	7585–39–9
Carbonic acid, monopotassium salt	298–14–6
Carbonic acid, monosodium salt (sodium bicarbonate)	144–55–8
Carnauba wax	8015–86–9
Carob gum (locust bean gum)	9000–40–2
Castor oil	8001–79–4
Castor oil, hydrogenated	8001–78–3
Cellulose	9004–34–6
Cellulose acetate	9004–35–7

Cellulose, carboxy methyl ether, sodium salt	9004–32–4
Cellulose, 2-hydroxyethyl ether	9004–62–0
Cellulose, 2-hydroxypropyl ether	9004–64–2
Cellulose, 2-hydroxypropyl methyl ether	9004–65–3
Cellulose, methyl ether	9004–67–5
Cellulose, mixture with cellulose carboxymethyl ether, sodium salt	51395–75–6
Cellulose, pulp	65996–61–4
Cellulose, regenerated	68442–85–3
Citric acid	77–92–9
Citric acid, 2-(acetyloxy)-, tributyl ester	77–90–7
Citric acid, calcium salt	7693–13–2
Citric acid, calcium salt (2:3)	813–94–5
Citric acid, dipotassium salt	3609–96–9
Citric acid, disodium salt	144–33–2
Citric acid, monohydrate	5949–29–1
Citric acid, monopotassium salt	866–83–1
Citric acid, monosodium salt	18996–35–5
Citric acid, potassium salt	7778–49–6
Citric acid, triethyl ester	77–93–0
Citric acid, tripotassium salt	866–84–2
Citric acid, tripotassium salt, monohydrate	6100–05–6
Citric acid, sodium salt	994–36–5
Citric acid, trisodium salt	68–04–2
Citric acid, trisodium salt, dihydrate	6132–04–3
Citric acid, trisodium salt, pentahydrate	6858–44–2
Coffee grounds	68916–18–7
Dextrins	9004–53–9
1,3-Dioxolan-2-one, 4-methyl-(propylene carbonate)	108–32–7
Fumaric acid	110–17–8
Gamma-cyclodextrin	17465–86–0

Gellan gum	71010–52–1
D-Glucitol (sorbitol)	50–70–4
Glycerol (glycerin) (1,2,3-propanetriol)	56–81–5
Guar gum	9000–30–0
Humic acid	1413–93–6
Humic acid, potassium salt	68514–28–3
Humic acid, sodium salt	68131–04–4
Lactic acid, n-butyl ester	138–22–7
Lactic acid, n-butyl ester, (S)	34451–19–9
Lactic acid, ethyl ester	97–64–3
Lactic acid, ethyl ester,(S)	687–47–8
Lanolin	8006–54–0
Lecithins	8002–43–5
Lecithins, soya	8030–76–0
Licorice Extract	68916–91–6
Maltodextrin	9050–36–6
Paper	None
Potassium chloride	7447–40–7
2-Propanol (isopropyl alcohol)	67–63–0
Red cabbage color, expressed from edible red cabbage heads via a pressing process using only acidified water	None
Silica, amorphous, fumed (crystalline free)	112945–52–5
Silica, amorphous, precipitated and gel	7699–41–4
Silica gel	63231–67–4
Silica gel, precipitated, crystalline-free	112926–00–8
Silica, hydrate	10279–57–9
Silica, vitreous	60676–86–0
Soap (The water soluble sodium or potassium salts of fatty acids produced by either the saponification of fats and oils, or the neutralization of fatty acid)	None
Sorbic acid, potassium salt	24634–61–5
Soapbark (Quillaja saponin)	1393–03–9

Sodium alginate	9005-38-3
Sodium chloride	7647-14-5
Syrups, hydrolyzed starch, hydrogenated	68425-17-2
Ultramarine blue (C.I. Pigment Blue 29)	57455-37-5
Urea	57-13-6
Vanillin	121-33-5
Xanthan gum	11138-66-2

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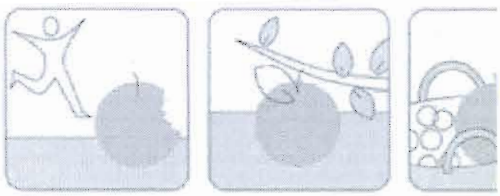

Pesticide EU-MRLs Database

Regulation (EC) No 396 / 2005

Products **Pesticides**

Updated on 25/11/2008

Disclaimer

This database is made available solely for the purpose of information. It has no legal value. It lists MRLs according to the Annexes of Regulation (EC) No 396/2005. The official MRLs are those published in the Official Journal of the European Union (Plant Protection - Pesticide Residues - Community Legislation). The Commission declines all responsibility or liability whatsoever for errors or deficiencies in this list. Neither the Commission nor any person acting on behalf of the Commission is responsible with regard to the improper use of the document and its contents.

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Pesticide residues and maximum residue levels (mg/kg)
(*) Indicates lower limit of analytical determination

Pesticides - Web Version - EU MRLs (File created on 04/12/2008 09:58)		
Code number	**Groups and examples of individual products to which the MRLs apply (a)**	**Repellants: Tall oil (++)**
100000	1. FRUIT FRESH OR FROZEN; NUTS	No MRL required
110000	(i) Citrus fruit	No MRL required
110010	Grapefruit (Shaddocks, pomelos, sweeties, tangelo, ugli and other hybrids)	No MRL required
110020	Oranges (Bergamot, bitter orange, chinotto and other hybrids)	No MRL required
110030	Lemons (Citron, lemon)	No MRL required
110040	Limes	No MRL required
110050	Mandarins (Clementine, tangerine and other hybrids)	No MRL required
110990	Others	No MRL required
120000	(ii) Tree nuts (shelled or unshelled)	No MRL required
120010	Almonds	No MRL required
120020	Brazil nuts	No MRL required
120030	Cashew nuts	No MRL required
120040	Chestnuts	No MRL required
120050	Coconuts	No MRL required
120060	Hazelnuts (Filbert)	No MRL required
120070	Macadamia	No MRL required
120080	Pecans	No MRL required
120090	Pine nuts	No MRL required
120100	Pistachios	No MRL required
120110	Walnuts	No MRL required
120990	Others	No MRL required
130000	(iii) Pome fruit	No MRL required
130010	Apples (Crab apple)	No MRL required
130020	Pears (Oriental pear)	No MRL required
130030	Quinces	No MRL required
130040	Medlar	No MRL required
130050	Loquat	No MRL required
130990	Others	No MRL required
140000	(iv) Stone fruit	No MRL required
140010	Apricots	No MRL required
140020	Cherries (sweet cherries, sour cherries)	No MRL required
140030	Peaches (Nectarines and similar hybrids)	No MRL required
140040	Plums (Damson, greengage, mirabelle)	No MRL required
140990	Others	No MRL required
150000	(v) Berries & small fruit	No MRL required
151000	(a) Table and wine grapes	No MRL required
151010	Table grapes	No MRL required
151020	Wine grapes	No MRL required
152000	(b) Strawberries	No MRL required
153000	(c) Cane fruit	No MRL required
153010	Blackberries	No MRL required
153020	Dewberries (Loganberries, Boysenberries, and cloudberries)	No MRL required
153030	Raspberries (Wineberries)	No MRL required

153990	Others	No MRL required
154000	(d) Other small fruit & berries	No MRL required
154010	Blueberries (Bilberries cowberries (red bilberries))	No MRL required
154020	Cranberries	No MRL required
154030	Currants (red, black and white)	No MRL required
154040	Gooseberries (Including hybrids with other ribes species)	No MRL required
154050	Rose hips	No MRL required
154060	Mulberries (arbutus berry)	No MRL required
154070	Azarole (mediteranean medlar)	No MRL required
154080	Elderberries (Black chokeberry (appleberry), mountain ash, azarole, buckthorn (sea sallowthorn), hawthorn, service berries, and other treeberries)	No MRL required
154990	Others	No MRL required
160000	(vi) Miscellaneous fruit	No MRL required
161000	(a) Edible peel	No MRL required
161010	Dates	No MRL required
161020	Figs	No MRL required
161030	Table olives	No MRL required
161040	Kumquats (Marumi kumquats, nagami kumquats)	No MRL required
161050	Carambola (Bilimbi)	No MRL required
161060	Persimmon	No MRL required
161070	Jambolan (java plum) (Java apple (water apple), pomerac, rose apple, Brazilean cherry (grumichama), Surinam cherry)	No MRL required
161990	Others	No MRL required
162000	(b) Inedible peel, small	No MRL required
162010	Kiwi	No MRL required
162020	Lychee (Litchi) (Pulasan, rambutan (hairy litchi))	No MRL required
162030	Passion fruit	No MRL required
162040	Prickly pear (cactus fruit)	No MRL required
162050	Star apple	No MRL required
162060	American persimmon (Virginia kaki) (Black sapote, white sapote, green sapote, canistel (yellow sapote), and mammey sapote)	No MRL required
162990	Others	No MRL required
163000	(c) Inedible peel, large	No MRL required
163010	Avocados	No MRL required
163020	Bananas (Dwarf banana, plantain, apple banana)	No MRL required
163030	Mangoes	No MRL required
163040	Papaya	No MRL required
163050	Pomegranate	No MRL required
163060	Cherimoya (Custard apple, sugar apple (sweetsop) , llama and other medium sized Annonaceae)	No MRL required
163070	Guava	No MRL required
163080	Pineapples	No MRL required
163090	Bread fruit (Jackfruit)	No MRL required
163100	Durian	No MRL required

163110	Soursop (guanabana)	No MRL required
163990	Others	No MRL required
200000	2. VEGETABLES FRESH OR FROZEN	No MRL required
210000	(i) Root and tuber vegetables	No MRL required
211000	(a) Potatoes	No MRL required
212000	(b) Tropical root and tuber vegetables	No MRL required
212010	Cassava (Dasheen, eddoe (Japanese taro), tannia)	No MRL required
212020	Sweet potatoes	No MRL required
212030	Yams (Potato bean (yam bean), Mexican yam bean)	No MRL required
212040	Arrowroot	No MRL required
212990	Others	No MRL required
213000	(c) Other root and tuber vegetables except sugar beet	No MRL required
213010	Beetroot	No MRL required
213020	Carrots	No MRL required
213030	Celeriac	No MRL required
213040	Horseradish	No MRL required
213050	Jerusalem artichokes	No MRL required
213060	Parsnips	No MRL required
213070	Parsley root	No MRL required
213080	Radishes (Black radish, Japanese radish, small radish and similar varieties)	No MRL required
213090	Salsify (Scorzonera, Spanish salsify (Spanish oysterplant))	No MRL required
213100	Swedes	No MRL required
213110	Turnips	No MRL required
213990	Others	No MRL required
220000	(ii) Bulb vegetables	No MRL required
220010	Garlic	No MRL required
220020	Onions (Silverskin onions)	No MRL required
220030	Shallots	No MRL required
220040	Spring onions (Welsh onion and similar varieties)	No MRL required
220990	Others	No MRL required
230000	(iii) Fruiting vegetables	No MRL required
231000	(a) Solanacea	No MRL required
231010	Tomatoes (Cherry tomatoes,)	No MRL required
231020	Peppers (Chilli peppers)	No MRL required
231030	Aubergines (egg plants) (Pepino)	No MRL required
231040	Okra, lady's fingers	No MRL required
231990	Others	No MRL required
232000	(b) Cucurbits - edible peel	No MRL required
232010	Cucumbers	No MRL required
232020	Gherkins	No MRL required
232030	Courgettes (Summer squash, marrow (patisson))	No MRL required
232990	Others	No MRL required
233000	(c) Cucurbits-inedible peel	No MRL required
233010	Melons (Kiwano)	No MRL required
233020	Pumpkins (Winter squash)	No MRL required
233030	Watermelons	No MRL required
233990	Others	No MRL required

234000	(d) Sweet corn	No MRL required
239000	(e) Other fruiting vegetables	No MRL required
240000	(iv) Brassica vegetables	No MRL required
241000	(a) Flowering brassica	No MRL required
241010	Broccoli (Calabrese, Chinese broccoli, Broccoli raab)	No MRL required
241020	Cauliflower	No MRL required
241990	Others	No MRL required
242000	(b) Head brassica	No MRL required
242010	Brussels sprouts	No MRL required
242020	Head cabbage (Pointed head cabbage, red cabbage, savoy cabbage, white cabbage)	No MRL required
242990	Others	No MRL required
243000	(c) Leafy brassica	No MRL required
243010	Chinese cabbage (Indian (Chinese) mustard, pak choi, Chinese flat cabbage (tai goo choi), peking cabbage (pe-tsai), cow cabbage)	No MRL required
243020	Kale (Borecole (curly kale), collards)	No MRL required
243990	Others ( )	No MRL required
244000	(d) Kohlrabi	No MRL required
250000	(v) Leaf vegetables & fresh herbs	No MRL required
251000	(a) Lettuce and other salad plants including Brassicacea	No MRL required
251010	Lamb´s lettuce (Italian cornsalad)	No MRL required
251020	Lettuce (Head lettuce, lollo rosso (cutting lettuce), iceberg lettuce, romaine (cos) lettuce)	No MRL required
251030	Scarole (broad-leaf endive) (Wild chicory, red-leaved chicory, radicchio, curld leave endive, sugar loaf)	No MRL required
251040	Cress	No MRL required
251050	Land cress	No MRL required
251060	Rocket, Rucola (Wild rocket)	No MRL required
251070	Red mustard	No MRL required
251080	Leaves and sprouts of Brassica spp (Mizuna)	No MRL required
251990	Others	No MRL required
252000	(b) Spinach & similar (leaves)	No MRL required
252010	Spinach (New Zealand spinach, turnip greens (turnip tops))	No MRL required
252020	Purslane (Winter purslane (miner's lettuce), garden purslane, common purslane, sorrel, glassworth)	No MRL required
252030	Beet leaves (chard) (Leaves of beetroot)	No MRL required
252990	Others	No MRL required
253000	(c) Vine leaves (grape leaves)	No MRL required
254000	(d) Water cress	No MRL required
255000	(e) Witloof	No MRL required
256000	(f) Herbs	No MRL required
256010	Chervil	No MRL required
256020	Chives	No MRL required

256030	Celery leaves (fennel leaves , Coriander leaves, dill leaves, Caraway leaves, lovage, angelica, sweet cisely and other Apiacea)	No MRL required
256040	Parsley	No MRL required
256050	Sage (Winter savory, summer savory,)	No MRL required
256060	Rosemary	No MRL required
256070	Thyme (marjoram, oregano)	No MRL required
256080	Basil (Balm leaves, mint, peppermint)	No MRL required
256090	Bay leaves (laurel)	No MRL required
256100	Tarragon (Hyssop)	No MRL required
256990	Others	No MRL required
260000	(vi) Legume vegetables (fresh)	No MRL required
260010	Beans (with pods) (Green bean (french beans, snap beans), scarlet runner bean, slicing bean, yardlong beans)	No MRL required
260020	Beans (without pods) (Broad beans, Flageolets, jack bean, lima bean, cowpea)	No MRL required
260030	Peas (with pods) (Mangetout (sugar peas))	No MRL required
260040	Peas (without pods) (Garden pea, green pea, chickpea)	No MRL required
260050	Lentils	No MRL required
260990	Others	No MRL required
270000	(vii) Stem vegetables (fresh)	No MRL required
270010	Asparagus	No MRL required
270020	Cardoons	No MRL required
270030	Celery	No MRL required
270040	Fennel	No MRL required
270050	Globe artichokes	No MRL required
270060	Leek	No MRL required
270070	Rhubarb	No MRL required
270080	Bamboo shoots	No MRL required
270090	Palm hearts	No MRL required
270990	Others	No MRL required
280000	(viii) Fungi	No MRL required
280010	Cultivated (Common mushroom, Oyster mushroom, Shi-take)	No MRL required
280020	Wild (Chanterelle, Truffle, Morel ,)	No MRL required
280990	Others	No MRL required
290000	(ix). Sea weeds	No MRL required
300000	3. PULSES, DRY	No MRL required
300010	Beans (Broad beans, navy beans, flageolets, jack beans, lima beans, field beans, cowpeas)	No MRL required
300020	Lentils	No MRL required
300030	Peas (Chickpeas, field peas, chickling vetch)	No MRL required
300040	Lupins	No MRL required
300990	Others	No MRL required
400000	4. OILSEEDS AND OILFRUITS	No MRL required
401000	(i) Oilseeds	No MRL required

401010	Linseed	No MRL required
401020	Peanuts	No MRL required
401030	Poppy seed	No MRL required
401040	Sesame seed	No MRL required
401050	Sunflower seed	No MRL required
401060	Rape seed (Bird rapeseed, turnip rape)	No MRL required
401070	Soya bean	No MRL required
401080	Mustard seed	No MRL required
401090	Cotton seed	No MRL required
401100	Pumpkin seeds	No MRL required
401110	Safflower	No MRL required
401120	Borage	No MRL required
401130	Gold of pleasure	No MRL required
401140	Hempseed	No MRL required
401150	Castor bean	No MRL required
401990	Others	No MRL required
402000	(ii) Oilfruits	No MRL required
402010	Olives for oil production	No MRL required
402020	Palm nuts (palmoil kernels)	No MRL required
402030	Palmfruit	No MRL required
402040	Kapok	No MRL required
402990	Others	No MRL required
500000	5. CEREALS	No MRL required
500010	Barley	No MRL required
500020	Buckwheat	No MRL required
500030	Maize	No MRL required
500040	Millet (Foxtail millet, teff)	No MRL required
500050	Oats	No MRL required
500060	Rice	No MRL required
500070	Rye	No MRL required
500080	Sorghum	No MRL required
500090	Wheat (Spelt Triticale)	No MRL required
500990	Others	No MRL required
600000	6. TEA, COFFEE, HERBAL INFUSIONS AND COCOA	No MRL required
610000	(i) Tea (dried leaves and stalks, fermented or otherwise of Camellia sinensis)	No MRL required
620000	(ii) Coffee beans	No MRL required
630000	(iii) Herbal infusions (dried)	No MRL required
631000	(a) Flowers	No MRL required
631010	Camomille flowers	No MRL required
631020	Hybiscus flowers	No MRL required
631030	Rose petals	No MRL required
631040	Jasmine flowers	No MRL required
631050	Lime (linden)	No MRL required
631990	Others	No MRL required
632000	(b) Leaves	No MRL required
632010	Strawberry leaves	No MRL required
632020	Rooibos leaves	No MRL required
632030	Maté	No MRL required
632990	Others	No MRL required
633000	(c) Roots	No MRL required
633010	Valerian root	No MRL required
633020	Ginseng root	No MRL required

633990	Others	No MRL required
639000	(d) Other herbal infusions	No MRL required
640000	(iv) Cocoa (fermented beans)	No MRL required
650000	(v) Carob (st johns bread)	No MRL required
700000	7. HOPS (dried) , including hop pellets and unconcentrated powder	No MRL required
800000	8. SPICES	No MRL required
810000	(i) Seeds	No MRL required
810010	Anise	No MRL required
810020	Black caraway	No MRL required
810030	Celery seed (Lovage seed)	No MRL required
810040	Coriander seed	No MRL required
810050	Cumin seed	No MRL required
810060	Dill seed	No MRL required
810070	Fennel seed	No MRL required
810080	Fenugreek	No MRL required
810090	Nutmeg	No MRL required
810990	Others	No MRL required
820000	(ii) Fruits and berries	No MRL required
820010	Allspice	No MRL required
820020	Anise pepper (Japan pepper)	No MRL required
820030	Caraway	No MRL required
820040	Cardamom	No MRL required
820050	Juniper berries	No MRL required
820060	Pepper, black and white (Long pepper, pink pepper)	No MRL required
820070	Vanilla pods	No MRL required
820080	Tamarind	No MRL required
820990	Others	No MRL required
830000	(iii) Bark	No MRL required
830010	Cinnamon (Cassia)	No MRL required
830990	Others	No MRL required
840000	(iv) Roots or rhizome	No MRL required
840010	Liquorice	No MRL required
840020	Ginger	No MRL required
840030	Turmeric (Curcuma)	No MRL required
840040	Horse-radish	No MRL required
840990	Others	No MRL required
850000	(v) Buds	No MRL required
850010	Cloves	No MRL required
850020	Capers	No MRL required
850990	Others	No MRL required
860000	(vi) Flower stigma	No MRL required
860010	Saffron	No MRL required
860990	Others	No MRL required
870000	(vii) Aril	No MRL required
870010	Mace	No MRL required
870990	Others	No MRL required
900000	9. SUGAR PLANTS	No MRL required
900010	Sugar beet (root)	No MRL required
900020	Sugar cane	No MRL required
900030	Chicory roots	No MRL required
900990	Others	No MRL required
1000000	10. PRODUCTS OF ANIMAL ORIGIN-TERRESTRIAL ANIMALS	No MRL required

1010000	(i) Meat, preparations of meat, offals, blood, animal fats fresh chilled or frozen, salted, in brine, dried or smoked or processed as flours or meals other processed products such as sausages and food preparations based on these	No MRL required
1011000	(a) Swine	No MRL required
1011010	Meat	No MRL required
1011020	Fat free of lean meat	No MRL required
1011030	Liver	No MRL required
1011040	Kidney	No MRL required
1011050	Edible offal	No MRL required
1011990	Others	No MRL required
1012000	(b) Bovine	No MRL required
1012010	Meat	No MRL required
1012020	Fat	No MRL required
1012030	Liver	No MRL required
1012040	Kidney	No MRL required
1012050	Edible offal	No MRL required
1012990	Others	No MRL required
1013000	(c) Sheep	No MRL required
1013010	Meat	No MRL required
1013020	Fat	No MRL required
1013030	Liver	No MRL required
1013040	Kidney	No MRL required
1013050	Edible offal	No MRL required
1013990	Others	No MRL required
1014000	(d) Goat	No MRL required
1014010	Meat	No MRL required
1014020	Fat	No MRL required
1014030	Liver	No MRL required
1014040	Kidney	No MRL required
1014050	Edible offal	No MRL required
1014990	Others	No MRL required
1015000	(e) Horses, asses, mules or hinnies	No MRL required
1015010	Meat	No MRL required
1015020	Fat	No MRL required
1015030	Liver	No MRL required
1015040	Kidney	No MRL required
1015050	Edible offal	No MRL required
1015990	Others	No MRL required
1016000	(f) Poultry -chicken, geese, duck, turkey and Guinea fowl-, ostrich, pigeon	No MRL required
1016010	Meat	No MRL required
1016020	Fat	No MRL required
1016030	Liver	No MRL required
1016040	Kidney	No MRL required
1016050	Edible offal	No MRL required
1016990	Others	No MRL required
1017000	(g) Other farm animals (Rabbit, Kangaroo)	No MRL required
1017010	Meat	No MRL required
1017020	Fat	No MRL required
1017030	Liver	No MRL required
1017040	Kidney	No MRL required
1017050	Edible offal	No MRL required

1017990	Others	No MRL required
1020000	(ii) Milk and cream, not concentrated, nor containing added sugar or sweetening matter, butter and other fats derived from milk, cheese and curd	No MRL required
1020010	Cattle	No MRL required
1020020	Sheep	No MRL required
1020030	Goat	No MRL required
1020040	Horse	No MRL required
1020990	Others	No MRL required
1030000	(iii) Birds' eggs, fresh preserved or cooked Shelled eggs and egg yolks fresh, dried, cooked by steaming or boiling in water, moulded, frozen or otherwise preserved whether or not containing added sugar or sweetening matter	No MRL required
1030010	Chicken	No MRL required
1030020	Duck	No MRL required
1030030	Goose	No MRL required
1030040	Quail	No MRL required
1030990	Others	No MRL required
1040000	(iv) Honey (Royal jelly, pollen)	No MRL required
1050000	(v) Amphibians and reptiles (Frog legs, crocodiles)	No MRL required
1060000	(vi) Snails	No MRL required
1070000	(vii) Other terrestrial animal products	No MRL required

Substance	**Legislation**	**Entry in to force**
Repellants: Tall oil (++)	Reg.(EC) N°149/2008	01/09/2008

Directorate-General for
Health & Consumers

FACTSHEET

New rules on pesticide residues in food

September 2008

Consumers are exposed to pesticides because small amounts can be found on harvested crops. These amounts are called pesticide residues. In the EU, from September 2008 onwards, a new Regulation[1] comes into force which lays down revised rules for pesticide residues

WHAT ARE PESTICIDES AND WHY ARE THEY USED?

- The yield of agricultural and horticultural crops can be **severely reduced as a result of infestation by pests and diseases**. In order to protect crops before and after harvest, plant protection products are used.

- In some cases these products act by confusing insects or making crops less palatable for pests. But more commonly, the damaging insects, weeds and fungi are killed by chemicals. **Such pesticides could have severe undesirable effects** if they are not strictly regulated.

- In the European Union no plant protection products can be used unless it has first been scientifically established that:

(1) They have no **harmful effects** on consumers, farmers or bystanders;

(2) They do not provoke unacceptable effects on the **environment**;

(3) They are sufficiently **effective**.

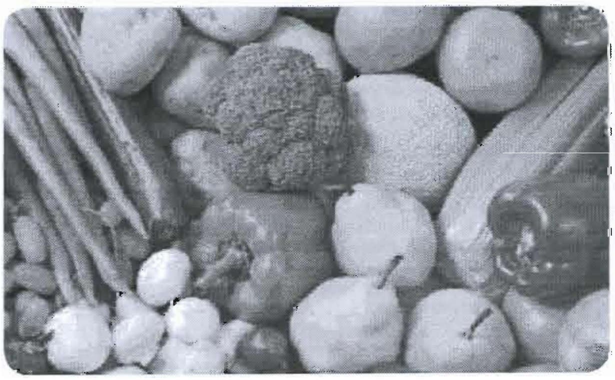
WHAT ARE MAXIMUM RESIDUE LEVELS (MRLs)?

- The amounts of residues found in food must be **safe for consumers** and must be **as low as possible**.

- A maximum residue level (MRL) is the highest level of a pesticide residue that is **legally tolerated** in or on food or feed.

- The **European Commission fixes MRLs** for all food and animal feed.

- The MRLs for all crops and all pesticides can be found in the **MRL database** on the Commission website.



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[1] *Regulation (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005.*

WHY REVISE THE EU RULES ON PESTICIDE RESIDUES?

- The **rules applicable before 1 September 2008 were complex**. For some pesticides, the Commission would set MRLs, for others, Member States were responsible. For some pesticides, the Commission could set MRLs, but the Member States could fix higher MRLs. And for some pesticides, no MRLs were set at all.

- **For traders and importers**, having to deal with 27 lists of national MRLs led to confusion about which MRL they had to respect.

- **For consumers**, the confusion led to concerns about the safety of pesticide residues in particular in cases where food exceeding the MRL in one Member State would be acceptable in other Member States.

WHAT IS IN THE NEW REGULATION?

- The new Regulation covers **all agricultural products intended for food or animal feed**. MRLs for 315 fresh products are listed, but these MRLs also apply to the same products after processing, adjusted to take account of dilution or concentration during the process.

- The Regulation covers pesticides currently or formerly used in agriculture in or outside the EU (around 1100). Where a pesticide is not specifically mentioned, a **general default MRL of 0.01 mg/kg applies**.

- The Regulation covers the **safety of all consumer groups, including, for example, babies, children and vegetarians**. The safety assessment for consumers is undertaken by the **European Food Safety Authority (EFSA)**, based on the toxicity of the pesticide, the maximum levels expected on food and the different diets of European consumers.

- The Regulation clearly designates the **role of the Member States, EFSA and the Commission** in the setting of MRLs and contains:

(1) The **EU MRLs** (about 45,000) already in force before September 2008;

(2) **The recently harmonised MRLs previously set by the Member States** (about 100,000);

(3) A list of low risk substances for which **MRLs are not necessary**.

HOW ARE MRLs FIXED?

- To ensure that MRLs are as low as possible, applicants seeking approval of a pesticide must submit scientific information about the minimum amounts of pesticide necessary to protect a crop and the residue level remaining on the crop after such treatment. The European Food Safety Authority (EFSA) then verifies that this residue is safe for all European consumer groups, including vulnerable groups such as babies, children and vegetarians. When there is a risk established for any consumer group, the MRL application will be rejected and the pesticide may not be used on that crop. Food safety thus has priority over plant protection.

- In many cases the amount of pesticide needed is much lower than the highest level that is still considered safe. In such cases the MRL is set at the lower level, thus ensuring that only the necessary (minimum) amount of pesticide is used.

- How and when the pesticide may be used is defined by the relevant national authority and can be found on the label of the pesticide. Authorisations are granted on a national basis because the local and environmental conditions and the occurrence of pests (and therefore uses of pesticides) may differ. For example, in the southern Member States where it is warmer, there are more insects and thus more insecticides are needed. In other parts of the EU, it is more humid – conditions that suit fungal infestation, and thus more fungicides are needed. When MRLs are set these differences should be taken into account.

- For crops grown outside the European Union, MRLs are set on request of the exporting country.

HOW ARE MRLs CONTROLLED AND ENFORCED?

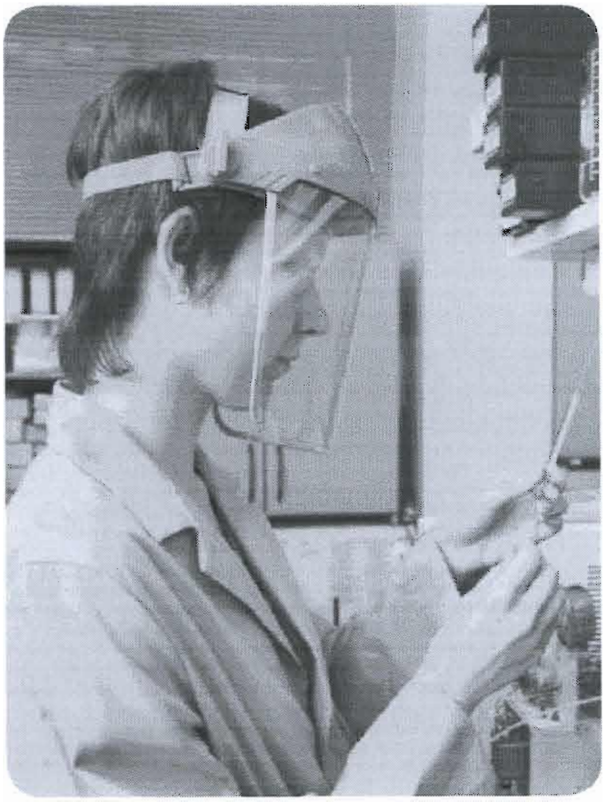
- Farmers, **traders and importers** are responsible for food safety, which includes compliance with MRLs. Member State authorities are responsible for control and enforcement of the MRLs. To ensure that this is done in an adequate and uniform way, the Commission has three instruments:

(1) The co-ordinated **EU multi-annual control programme** sets out for each Member State the main pesticide-crop combinations to monitor and the minimum numbers of samples to take. Member States have to report the results, which are published in an annual report.

(2) **Community Reference Laboratories** co-ordinate, train staff, develop methods of analysis and organise tests to evaluate the skills of the different national control laboratories.

(3) **The Food and Veterinary Office** of the Commission carries out inspections in the Member States to assess and audit their control activities.

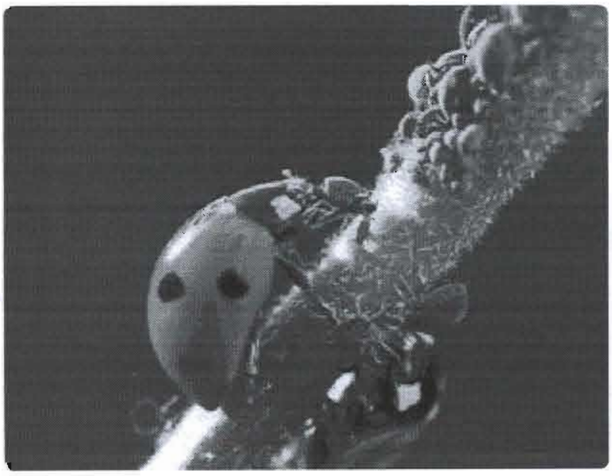
- If pesticide residues are found at a level of concern for consumers, the **Rapid Alert System for Food and Feed** (RASFF) circulates the information and measures are taken to protect the consumer.



WHAT IS THE EU DOING TO REDUCE THE USE OF PESTICIDES?

- In addition to working to ensure that consumers and animals are protected from pesticide residues in food and feed, the EU seeks to **reduce the overall impact of pesticides on health and the environment** and indeed their actual usage. In 2006, the European Commission proposed a strategy to improve the way pesticides are used across the EU

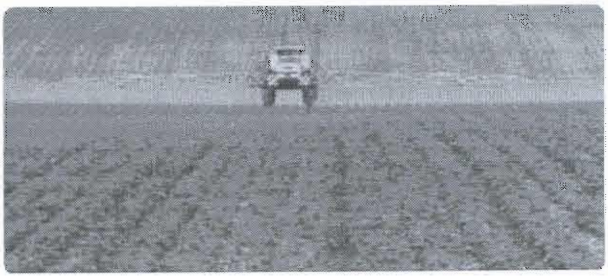
- The strategy aims to **encourage low-input or pesticide-free cultivation**, in particular through raising user awareness, promoting the use of codes of good practice and making financial means available for applied research and training.



- In 2006 the Commission made **two legal proposals** which are currently being discussed by the European Parliament and the Council:

(1) The first proposal is for a Regulation on placing on the market of plant protection products. This would specify **strict criteria for approval** to ensure a high level of protection for human and animal health and the environment. It would also establish a mechanism for **substitution of more toxic pesticides** by safer (including non-chemical) alternatives.

(2) The second proposal is for a **Directive on the sustainable use of pesticides**. This proposal aims at reducing the risk which is linked to the use of pesticides, improving the quality and efficacy of pesticide application equipment, ensuring better training and education of users and developing integrated pest management schemes.



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FOR FURTHER INFORMATION

- General information on pesticide residues
  http://ec.europa.eu/food/plant/protection/pesticides/index_en.htm
- EU Pesticide Residues monitoring Report
  http://ec.europa.eu/food/fvo/specialreports/pesticides_index_en.htm
- FVO-inspections
  http://ec.europa.eu/food/fvo/index_en.htm
- RASFF
  http://ec.europa.eu/food/food/rapidalert/index_en.htm
- European Food Safety Authority
  http://www.efsa.europa.eu
- Community Reference Laboratories for pesticide residues
  http://www.crl-pesticides.eu

THE MRL DATABASE

- To find out which MRL is applicable for which crop and which pesticide, a database can be consulted on the website of the European Commission. With a user friendly search tool the MRLs can be viewed by crop, by crop group, by crop code or by pesticide in all EU languages. A link is made to the legislation where the MRL is adopted and the history of changes to the MRLs can be followed. The information can be exported in excel format.

  http://ec.europa.eu/sanco_pesticides/public/index.cfm

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