Distilled Tall Oil

Crops

Identification of Petitioned Substance

Chemical Names:
Distilled tall oil
Crude tall oil
Tall oil

Other Name:
Tallol
DTO
CTO
Liquid rosin
Tall oil acid

Trade Names:
Altapyne® M-28B
Actinol EPG
Actinol FA-1
Actinol FA-2
Pamak 4

CAS Numbers:
8002-26-4 (for either crude or distilled tall oil)

Other Codes:
EC No. 232-304-6
UNII No. 1 GX6Z36A79

Summary of Petitioned Use

Ingevity Corporation petitioned the United States Department of Agriculture (USDA) National Organic Program (NOP) for the addition of distilled tall oil to the National List as a synthetic substance approved for use in organic crop production (USDA 2020a). This petition includes the use of distilled tall oil as an inert substance for use as a solvent, sticker, anti-leaching agent, and time-release agent in pesticides for crop production. In response to the petition by the Ingevity Corporation, the National Organic Standards Board (NOSB) Materials Subcommittee has requested a technical report focused on distilled tall oil for crop production.

A technical report on tall oil was submitted to the NOP in 2010 in response to a petition by Biomor Israel Ltd. for the addition of tall oil to the National List (USDA 2008, USDA 2010). The NOSB reviewed the tall oil technical report in 2010 and recommended that the substance not be added to the National List (NOSB 2010). The NOSB recommendation stated:

> Tall oil fails criteria categories 1 [adverse impacts on humans or the environment?], 2 [is the substance essential to organic production?], and 3 [is the substance compatible with organic production practices?]. Even though tall oil is being petitioned as an inert, it also has insecticidal properties and so fails the environmental impact criteria. There are alternatives, therefore it fails the essentiality criteria, and because of its insecticidal properties it is not compatible or consistent with organic or sustainable agriculture.

Characterization of Petitioned Substance

Crude Tall Oil vs Distilled Tall Oil

Crude tall oil and distilled tall oil are complex mixtures of compounds derived from coniferous trees. Both crude and distilled tall oil are comprised of the same three classifications of compounds: fatty acids, rosin acids (also referenced as rosin or resin acids), and neutrals (also referenced as unsaponifiable compounds) (Wansbrough, Cousin 1987, Huibers 1997, USDA 2010, EFSA 2012, EPA 2021). In both crude and distilled tall oil, neutrals make up the smallest portion of the mixture, accounting for less than 20%, and often less than 10% of the total mixture (Huibers 1997, USDA 2010, EFSA 2012).

Crude tall oil is differentiated from distilled tall oil based on the amount of refinement of the mixture, although both substances share the same Chemical Abstracts Service (CAS) number (8002-26-4) (USDA 2010, HC 2019). The difference between crude and distilled tall oil is based on purification via fractional distillation processes (Huibers 1997, HC 2019, EPA 2021). Distillation typically reduces the percentage of neutrals and rosin acids, enriching the fatty acid composition in distilled tall oil compared to the crude precursor (Magee and Zinkel 1992, USDA 2010, Lappi and Alén 2011). However, the specific differences between crude and distilled tall oils vary based on the species of tree being processed, the specific pulping conditions used to produce the black liquor feedstock, and the distillation parameters (Huibers 1997, HC 2019). While crude and distilled tall oil share many characteristics and have a similar chemical composition, "nearly all U.S. tall oil is distilled" (Magee and Zinkel 1992, EPA 157149).

Composition of the Substance:

Tall oil (both crude and distilled) has been classified as a substance of Unknown or Variable Composition, Complex Reaction Products or Biological Materials (UVCB) (HC 2019). As described above in the "Crude Tall Oil vs Distilled Tall Oil" section, tall oil is comprised of three main categories of compounds: fatty acids, rosin acids, and neutrals (Cousin 1987, Huibers 1997, USDA 2010, EPA 2021). All three categories include a range of compounds, with their specific make-up dependent on the species of tree being processed and the processing conditions (Cousin 1987, Huibers 1997, EFSA 2012). The composition ranges of crude and distilled tall oil are listed below in Table 1.

Table 1. Typical composition of crude and distilled tall oil

Category of compounds	Crude tall oil	Distilled tall oil
Fatty acids	30-68%	17-70%
Rosin acids	26-60%	25-77%
Neutrals	5-38%	1.9-19%

Sources: Wansbrough, Magee and Zinkel 1992, Huibers 1997, USDA 2010, Lappi and Alén 2011, Aro and Fatehi 2017, HC 2019, Vevere et al. 2020.

Fatty acids are long chains of hydrocarbons (typically between 12 and 20 carbons) which include a carboxylic acid functional group (Magee and Zinkel 1992, Huibers 1997, Timberlake 2016, Vevere et al. 2020, Wan and Wang 2020). Fatty acids found in distilled tall oil include both saturated (carbon – carbon single bonds) and unsaturated fatty acids (carbon – carbon double bond). The most common fatty acids found in crude and distilled tall oil are listed below in Table 2. Their chemical structures are shown below in Figure 1.

Table 2. Common fatty acids in crude and distilled tall oil

Fatty acid	Chemical formula	Molecular weight	Percent of crude tall oil fatty acids	Percent of distilled tall oil fatty acids
Oleic acid	$C_{18}H_{34}O_2$	282.468 g/mol	9.1-16.3%	2.4-26.2%
Linoleic acid	$C_{18}H_{32}O_2$	280.452 g/mol	30.5-38%	1.9-39.8%
Palmitic acid	$C_{16}H_{32}O_2$	256.430 g/mol	~3%	0.2-2.9%

Sources: Wansbrough, Magee and Zinkel 1992, Huibers 1997, USDA 2010, Robinson et al. 2009, Lappi and Alén 2011, HC 2019, ECHA 2021.

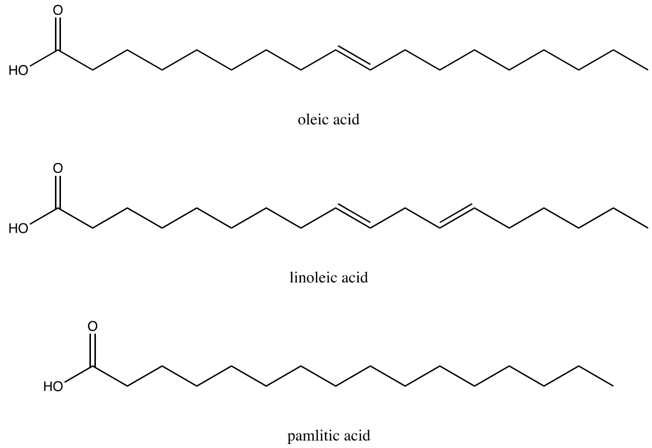


Figure 1

Rosin acids commonly include tricyclic carbon rings made of between 18 and 20 carbons that include a carboxylic acid functional group (Magee and Zinkel 1992, Huibers 1997, Vevere et al. 2020, Wan and Wang 2020). Rosin acids typically have higher boiling points than the fatty acid components of tall oil (Huibers et al. 1997). The most common rosin acids found in crude and distilled tall oil are listed below in Table 3. Their chemical structures are shown below in Figure 2.

Table 3. Common rosin acids in crude and distilled tall oil

Resin acid	Chemical formula	Molecular weight	Percent of crude tall oil rosin acids	Percent of distilled tall oil rosin acids
Abietic acid	$C_{20}H_{30}O_2$	302.458 g/mol	11.1-19.2%	1.9-33.4%
Dehydroabietic acid	$C_{20}H_{28}O_2$	300.4 g/mol	not reported	1.2-16.4%
Primaric acid	$C_{20}H_{30}O_2$	302.458 g/mol	4.7-8.2%	2.6-27.3%
Isoprimaric acid	$C_{20}H_{30}O_2$	302.458 g/mol	not reported	1.9-11.1%

Sources: Wansbrough, Magee and Zinkel 1992, Huibers 1997, USDA 2010, Lappi and Alén 2011, HC 2019, ECHA 2021.

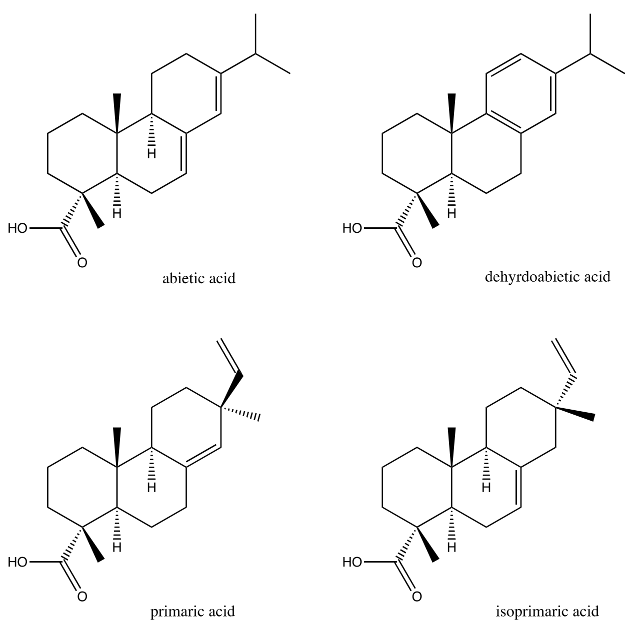


Figure 2

Neutral compounds found in crude and distilled tall oil have not been characterized and reported to the extent of fatty and rosin acid components (USDA 2010, HC 2019). Neutrals make up a small portion of distilled tall oil and include any chemical compound that is unaffected by changes to the pH of the solution (i.e., does not include a carboxylic acid functional group) (Wansbrough, Huibers 1997, EFSA 2012). Neutrals may include a wide range of chemical compounds, although alkanes (hydrocarbons), steroid-type compounds, ketones, aldehydes, alcohols, mercaptans, and salts have all been found within the neutral class of substances in tall oil (Wansbrough, Cousin 1987, Huibers 1997, Cantrill 2008, USDA 2010, Lappi and Alén 2011, EFSA 2012, Aro and Fatehi 2017, HC 2019, Vevere et al. 2020 EPA 2021).

Source or Origin of the Substance:

Distilled tall oil is isolated as a byproduct from black liquor, which is formed in the alkaline conditions of Kraft pulping of coniferous trees (Wansbrough, Lappi and Alén 2011, Aro and Fatehi 2017, Vevere et al. 2020). Tall oil soap is isolated from black liquor by skimming or decantation to prevent scaling of pulping equipment and the black liquor is returned to the pulping stream for further processing (Wansbrough, Huibers 1997, Aro and Fatehi 2017). The tall oil soap is reacted with an acid, usually sulfuric acid (H_2SO_4), to form crude tall oil which undergoes further purification via distillation to produce distilled tall oil (Wansbrough, Huibers 1997, Aro and Fatehi 2017, Vevere et al. 2020).

Properties of the Substance:

The properties of distilled tall oil vary based on the species of tree it is derived from and its production conditions (as described above in "Composition of the Substance"). General properties of distilled tall oil are displayed below in Table 4.

Table 4. Properties of distilled tall oil

Property	Distilled tall oil
CAS No.	8002-26-4
Physical appearance	Viscous liquid yellow to amber/brown in color
Relative density	0.949
Solubility	Insoluble in water, soluble in most organic solvents
Melting point	0.15 °C
Boiling point	360.15 °C

Sources: EPA 157149, Wansbrough, Huibers 1997, Robinson et al. 2009, WR 2015, Aro and Fatehi 2017, IC 2019, Vevere et al. 2020.

Specific Uses of the Substance:

Distilled tall oil has many applications across industries, including soap, disinfectant, sanitizer, cutting oil, oil in textile production, metal polish, biofuel precursor, and a source of polymeric material (Wansbrough, Lappi and Alén 2011, Aro and Fatehi 2017, Vevere et al. 2020). In livestock production, distilled tall oil has been used in feed formulations to reduce methane production from ruminants (EPA 2017a, Vuorenmaa and Kettunen 2017). Distilled tall oil is used in crop production as both an active and inert ingredient in pesticides for crop production (Xie and Isman 1995, EFSA 2012, EPA 2017a, Wan and Wang 2020).

The applications of distilled tall oil in pesticide formulations will be the focus of this section.

Active ingredient – pesticides

Oils, such as distilled tall oil, are most effective against soft-bodied insects and are thought to be primarily active by physical suffocation of pests (Cousin 1987, Xie and Isman 1995, Brogán et al. 2006, USDA 2019, Wan and Wang 2020, USDA 2021). When used as an active ingredient in pesticides distilled tall oil is most effective against larvae and is less effective against adult insects (Xie and Isman 1995).

Inert ingredient – pesticides

In addition to being an active ingredient in oil pesticides, distilled tall oil can be used as an inert ingredient. The categorization of distilled tall oil as an inert ingredient in pesticide formulations does not preclude it from having pesticidal character when used as an inert. This is explicitly described by the EPA, which states that "the term "inert" is not intended to imply nontoxicity; the ingredient may or may not be chemically active" (EPA 2017a). The inert ingredient classification from the EPA distinguishes active from inert ingredients "with respect to pesticidal activity," particularly whether "when used as directed at the proposed dilution [the substance can] function as a pesticide," as described in 40 CFR 153.125. Based on these criteria, a substance may be the active ingredient of a pesticide in one formulation but may be classified as an inert in another formulation in which it no longer has pesticidal activity due to dilutions or chemical combinations, and serves a different purpose (i.e., solvent, surfactant, etc.).

When used as petitioned by Ingevity Corporation, distilled tall oil is classified as an inert. Distilled tall oil acts as an inert solvent to dissolve active ingredients for application to crops (USDA 2020a, Wan and Wang 2020).

In addition to acting as a solvent, Ingevity Corporation has also described inert applications for distilled tall oil as a sticker, anti-leaching agent, and time release agent (USDA 2020a). In these applications, the hydrophobic nature of distilled tall oil decreases the water solubility of the pesticide formulations and gives longer residence times once applied to crops (USDA 2020a). The hydrophobic nature of distilled tall oil also prevents the substance and dissolved active ingredients from leaching into groundwater. The petition also claims that distilled tall oil present in topsoil may prevent leaching of micronutrients, such as zinc (Zn^{2+}) (USDA 2020a).

Inert ingredient – fertilizers

The hydrophobic nature of distilled tall oil may provide time-releasing properties to fertilizer formulations. In this application, fertilizer may be encapsulated in a film of distilled tall oil to prevent the fertilizer leaching from the soil and only release fertilizer as the film is metabolized by soil organisms (USDA 2020a).

<u>Approved Legal Uses of the Substance:</u>

The USDA states that "tall oil rosin" shall refer to a source of rosin used in naval stores, which describes "the kind of rosin remaining after the removal of fatty acids from tall oil by fractional distillation, and having the characteristic form and appearance and other physical and chemical properties normal for other kinds of rosin" (7 CFR 160.12 and §160.3).

The United States Food and Drug Administration (FDA) has designated tall oil as an "indirect food substance affirmed as generally recognized as safe (GRAS)" (21 CFR 186.1557). In this affirmation, the FDA describes tall oil as "essentially the sap of the pine tree…obtained commercially from waste liquors of pinewood pulp mills and consists mainly of tall oil resin acids and tall oil fatty acids." The FDA has affirmed the GRAS status of tall oil when "the ingredient is used as a constituent of cotton and cotton fabrics used for dry food packaging."

The FDA allows the use of tall oil and derivative substances for a range of applications in food production and food packaging. Tall oil is permitted by the FDA in food production as:

- a component of drying oils in finished rosins food ingredients in §181.26
- a component of sanitizing solutions in §178.1010
- a defoaming agent in food coatings in §176.200 and §173.340

Tall oil is permitted by the FDA in food packaging as:

- tall oil rosin in various packaging components in §178.3870
- an antioxidant and/or stabilizer in polymer formulations in §178.2010

- a component of paper and paperboard packaging in §176.170 and §176.210
- a component of textiles and textile fibers for food packaging in §177.2800
- a component of rubber articles used in food production or packaging in §177.2600
- a component of cellophane for food packaging in §177.1200
- a component of adhesives used in food packaging in §175.105
- a drying oil in resinous and polymeric coatings in §175.300 and §175.320

The United States Environmental Protection Agency (EPA) has listed tall oil as an "inert ingredient used pre- and post-harvest [that is exempted] from the requirement of a tolerance." Tall oil, tall oil fatty acids, and tall oil rosin are exempted from pesticide tolerances when used as a "surfactant, related adjuvants of surfactants [and as a] solvent/carrier" in 40 CFR 180.910. Tall oil is listed on EPA List 3, inerts of unknown toxicity. Neither tall oil nor distilled tall oil is listed on EPA List 4, minimal risk inert ingredients. Additionally, both List 3 and List 4 include many specific tall oil fatty acid compounds and derivatives.

Action of the Substance:

The mode of action applications of distilled tall oil in pesticide formulations is discussed below based on its application within the pesticide.

Active ingredient

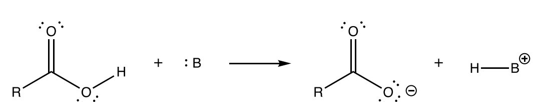
Distilled tall oil disrupts cellular respiration by suffocation (Cousin 1987, Xie and Isman 1995, Brogán et al. 2006, USDA 2019, Wan and Wang 2020, USDA 2021). When soft-bodied insects are coated with distilled tall oil the transport of oxygen and other metabolites across the cellular membrane is disrupted, causing cell death in the insect (Brogán et al. 2006). The application of oils to insects may also disrupt cellular membranes and rupture cells (Brogán et al. 2006). However, Xie and Isman have reported that distilled tall oil is more potent than other oil-based pesticides, suggesting that distilled tall oil may have additional, chemically based toxicity when applied to the aphid *Myzus persicae* (Xie and Isman 1995).

Inert ingredient

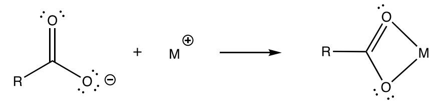
As a solvent in pesticide formulations the hydrophobic nature, and low water solubility, of the substance allows for the dissolution of compounds that are unable to be dissolved in water such as nonpolar pesticide ingredients, both active and inert. The incorporation of polar groups in the carboxylic acid functionality present on both fatty and rosin acids allows for the potential interaction with both polar and nonpolar compounds in pesticide formulations (Silberberg 2003, Timberlake 2016).

Furthermore, the hydrophobic nature of distilled tall oil makes it useful for inert applications as a sticker, anti-leaching agent, and time-release agent. Since distilled tall oil has low solubility in water, it is unlikely to be washed off applied crops, from topsoil, or from encapsulated substances when exposed to precipitation or irrigation. The action of distilled tall oil as a solvent in agricultural formulations will also prevent undesired migration of dissolved substances, provided that they are unable to effectively migrate into aqueous solutions.

The carboxylic acid functional groups can undergo deprotonation by a base (:B) to yield a carboxylate anion, as described below in Equation 1 (Silberberg 2003, Timberlake 2016). Once the carboxylate anion is formed, the carboxylate anion can form a chelate complex to metal ions by donation of non-bonding oxygen electrons, as described below in Equation 2 (Shiver and Atkins 2008).



Equation 1



Equation 2

Upon metal chelation (product of Equation 2), the character of the metal ion (i.e., micronutrient) is changed from its initial ionic form (M^+). The hydrophobic nature of the compounds in distilled tall oil would be transferred to chelated metals, which would decrease their water solubility and the potential to leach from the soil (Shriver and Atkins 2008).

Combinations of the Substance:

When used as petitioned, distilled tall oil would be combined with various other compounds, both active and inert ingredients of pesticide formulations (USDA 2020a). When used as an active ingredient, these combinations may include water as a solvent, as well as additional surfactants to promote the dispersion of the hydrophobic distilled tall oil in aqueous solution (Cousin 1987).

When used as an inert ingredient, distilled tall oil would be combined with the active pesticide or herbicide compound(s) (USDA 2020a, Wan and Wang 2020). The pesticide formulation may also include co-solvents, added to adjust the viscosity of the solution. These co-solvents could include a wide range of organic solvents including glycols (e.g., ethylene glycol, propylene glycol, etc.), halogenated hydrocarbons (e.g., dichloromethane, dichloroethane, etc.), polar aprotic solvents (e.g., acetonitrile, dimethylacetamide, etc.), ethers (e.g., tetrahydrofuran [THF], diethyl ether, etc.), aliphatic hydrocarbons (alkanes; e.g., paraffin and mineral oils), and aromatic hydrocarbons (e.g., xylene, alkyl naphthalenes, etc.) (Wan and Wang 2020). When additional co-solvents are included in the formulation, pesticides with distilled tall oil may also include a surfactant, which may be of an anionic, cationic, or non-ionic nature (Wan and Wang 2020). As described above in “Action of the Substance,” surfactants are compounds that include hydrophobic and hydrophilic portions to improve mixing of dissimilar materials. There may also be other inert compounds added to formulations that serve as emulsifiers, defoamers, stabilizers, wetting agents, anti-microbial agents, anti-freeze agents, pigments and colorants, and buffers (Wan and Wang 2020).

Status

Historic Use:

Distilled tall oil has no historic use in organic agriculture. Distilled tall oil and other products of crude tall oils have been used as active and inert ingredients of pesticides and herbicides in conventional agriculture (Cousin 1987, Wan and Wang 2020). Additionally, the hydrophobic nature of distilled tall oil has been used as a treatment and waterproofing agent in maritime production, such as sails and decking, and paper and ink production (Wansbrough, Vevere et al. 2020).

Organic Foods Production Act, USDA Final Rule:

Tall oil is not listed in Organic Foods Production Act of 1990 (OFPA) or the USDA organic regulations, 7 CFR Part 205. The USDA offers exemptions that meet the requirements outlined in 7 U.S.C. 6517, including “for substances that are otherwise prohibited [when the substance] is used in production and contains synthetic inert ingredients that are not classified by the Administrator of the Environmental Protection Agency as inerts of toxicological concern.”

Tall oil is listed on EPA List 3, inerts of unknown toxicity. Neither tall oil nor distilled tall oil is listed on (a) EPA List 4, minimal risk inert ingredients or on (b) EPA List 1, inert ingredients of toxicological concern.

International

Canadian General Standards Board Permitted Substances List -

This list was updated in March 2021.Tall oil is not listed in the CAN/CGSB-32.311-2020.

CODEX Alimentarius Commission, Guidelines for the Production, Processing, Labelling and Marketing of Organically Produced Foods (GL 32-1999) -

Tall oil is not listed in the CODEX GL 32-1999.

European Economic Community (EEC) Council Regulation, EC No. 834/2007 and 889/2008

Tall oil is not listed in EC No. 834/2007 or EC No. 889/2008.

Japan Agricultural Standard (JAS) for Organic Production—

Tall oil is not listed in the JAS for Organic Production.

International Federation of Organic Agriculture Movements (IFOAM) –

Tall oil is not listed in the IFOAM.

Evaluation Questions for Substances to be used in Organic Crop or Livestock Production

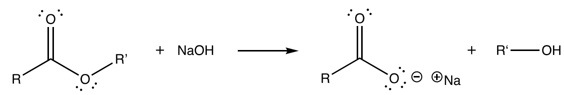
Evaluation Question #1: Indicate which category in OFPA that the substance falls under: (A) Does the substance contain an active ingredient in any of the following categories: copper and sulfur compounds, toxins derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treated seed, vitamins and minerals; livestock parasiticides and medicines and production aids including netting, tree wraps and seals, insect traps, sticky barriers, row covers, and equipment cleansers? (B) Is the substance a synthetic inert ingredient that is not classified by the EPA as inerts of toxicological concern (i.e., EPA List 4 inerts) (7 U.S.C. § 6517(c)(1)(B)(ii))? Is the synthetic substance an inert ingredient which is not on EPA List 4, but is exempt from a requirement of a tolerance, per 40 CFR part 180?

A) Distilled tall oil is a horticultural oil. Distilled tall oil has livestock applications as a feed additive and as active and inert ingredients in pesticide, herbicide, and fertilizer formulations (Cousin 1987, Xie and Isman 1995, USDA 2010, Vuorenmaaa and Kettunen 2017, USDA 2020a, Wan and Wang 2020).

B) Distilled tall oil is not specifically listed on EPA List 4. However, there are many compounds listed as specific tall oil fatty acids on EPA List 4. Additionally, the EPA has listed tall oil as an "inert ingredient used pre- and post-harvest [that is exempted] from the requirement of a tolerance" in 40 CFR 180.910.

Evaluation Question #2: Describe the most prevalent processes used to manufacture or formulate the petitioned substance. Further, describe any chemical change that may occur during manufacture or formulation of the petitioned substance when this substance is extracted from naturally occurring plant, animal, or mineral sources (7 U.S.C. § 6502 (21)).

Distilled tall oil is a substance that is isolated and refined from the Kraft pulping process of coniferous trees. The Kraft process produces alkaline conditions (pH ~9) via the addition of sodium hydroxide (NaOH) (Vevere et al. 2020). The alkaline conditions of the Kraft process break down the main components of trees (cellulose, hemicellulose, and lignin) via saponification (base-catalyzed hydrolysis) of esters (reactant), as shown below in Equation 3. The hydrolysis of the ester linkage produces the sodium salt of a carboxylate anion (soap) and an alcohol (Timberlake 2016).



Equation 3

The neutralization of rosin and fatty acids produced via neutralization by sodium hydroxide (Equation 1 in "Action of the Substance") and those produced by ester hydrolysis (Equation 3) make up tall oil soap. Tall oil soap is found within a more complex mixture of hydrolyzed cellulose, hemicellulose, and lignin structures, collectively known as black liquor. Once tall oil soaps are formed in the Kraft pulping process, they must be removed to prevent scaling of the pulping machinery (Aro and Fatehi 2017).

The removal of tall oil soap from black liquor is the first step in the production of distilled tall oil, as outlined below in Figure 3 (Aro and Fatehi 2017). In this process the tall oil soap salts crystallize out of the nonpolar black liquor mixture and form soap solids that float to the top of the viscous mixture (Wansbrough, Aro and Fatehi 2017). The soap solids are removed from the rest of the black liquor through physical seperation means, usually either by skimming or decanting them from the mixture. In this process some non-tall oil soap salts are trapped in the precipitating solids, along with various hydrocarbons, sterols, lignin and lignate salts, sodium sulfate and sodium carbonate, mercaptans and other compounds that make up the neutral class of compounds in tall oils (Wansbrough, Huibers 1997, Aro and Fatehi 2017, Vevere et al. 2020). Additionally, some tall oil soap remains trapped in the black liquor, which has been estimated to be approximately 20-40% of the total amount of tall oil soap initially present in the black liquor (Aro and Fatehi 2017, Vevere et al. 2020).

In some processes, polymers are added to the black liquor as flocculants (Huibers 1997, Aro and Fatehi 2017). The addition of polymeric flocculants facilitates the aggregation and separation of tall oil soap salts from black liquor by binding to the hydrophilic portion of the salt. While the addition of polymers improves the separation of tall oil soap from black liquor, their interaction with the carboxylate group of the soap interferes with the acidulation process and may complicate the recycling of spent acid solutions (Aro and Fatehi 2017).

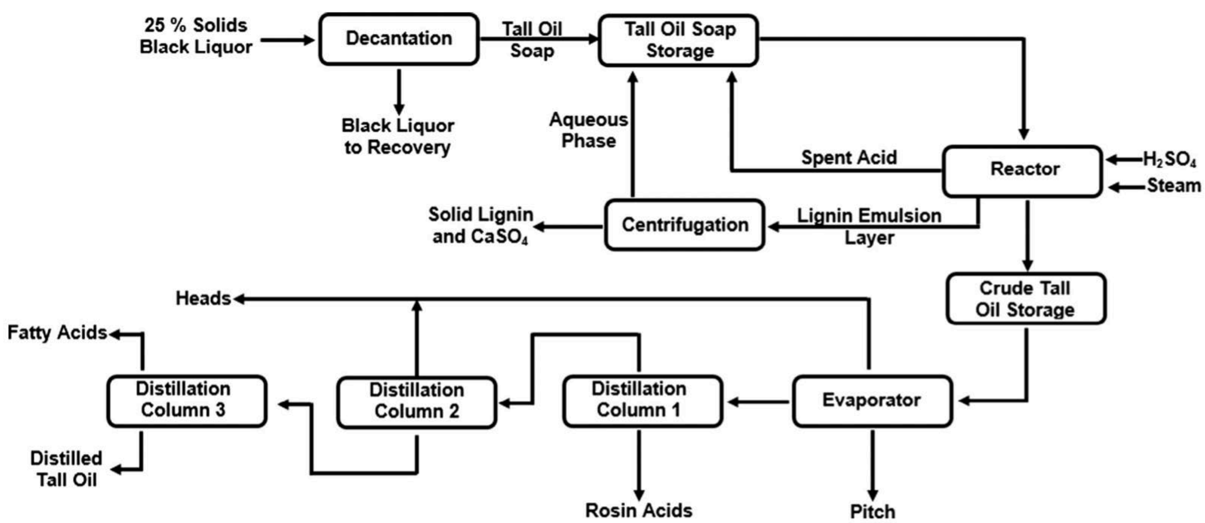
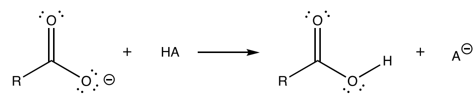


Figure 3

Once the tall oil soap is removed from the black liquor, it is placed in a storage tank (Aro and Fatehi 2017). The acidulation process, converting tall oil soap to crude tall oil, begins in the initial storage of the tall oil soap, which is combined with the weakly acidic mixture of spent acid. In some cases, the aqueous phase isolated from the lignin emululsion produced during the acidulation process is also added to the soap storage and initial conversion to crude tall oil, as shown in Figure 3 (Wansbrough, Aro and Fatehi 2017).

After initial treatment in the tall oil soap storage container, the soap mixture is moved to the reactor where it undergoes the acidulation process. In this process the soap salts are reacted with an acid to generate neutral rosin and fatty acids, as shown below in Equation 4 (Wansbrough, Huibers 1997, Silberberg 2003, Timberlake 2016, Aro and Fatehi 2017). The acidulation process generally uses concentrated sulfuric acid (H_2SO_4) or boric acid (H_3BO_3) to generate a solution with a pH of 3-4 (Wansbrough, Huibers 1997, Aro and Fatehi 2017, Vevere et al. 2020). Sulfuric acid is more common in the acidulation process due to financial considerations, and its higher reactivity and yields. Steam is used to heat the mixutre and increase the rate of reaction (Wansbrough, Aro and Fatehi 2017). The acidulation process has an estimated conversion and isolation of 75-90% of the tall oil soap into crude tall oil (Huibers 1997).



Equation 4

The rosin and fatty acids produced in the acidulation process are no longer charged and become insoluble in water. The formation of hydrophobic products results in the formation of a multiphasic product, which is left to stand overnight to aid in the separation of liquid phases (Wansbrough, Aro and Fatehi 2017). The acidulation product forms two main layers that separate tall oil soap from neutral components and contaminants: the hydrophobic organic layer which is comprised of the crude tall oil, and the polar aqueous layer with the spent sulfate and hydrogen sulfate salts (Wansbrough, Huibers 1997, Aro and Fatehi 2017). Between the two layers is an emulsion, which is a combination of the organic and aqueous layers that have been dispersed into a colloidal state (Godman 1982). The emulsion also contains lignin and calcium lignate solids, which are removed from the emulsion via centrifugation. The aqueous separation from the emulsion is added to the tall oil soap storage container, along with the spent acid from the reactor, while the solid lignin and calcium lignate compounds are sent back to the Kraft pulping process to be used as an energy source (Huibers 1997, Aro and Fatehi 2017).

The acidulation process produces crude tall oil in a 95-98% yield as a mixture that contains a small number of impurities, typically trace water, lignin, and other neutrals (Wansbrough, Aro and Fatehi 2017). Once isolated, crude tall oil is refined through distillation-based purification processes to isolate rosin and fatty acids (with a minimum of 90% purity) and distilled tall oil, as shown above in Figure 3. The evaporation and distillation processes are done under vacuum to prevent decomposition of high-boiling compounds (Wansbrough, Huibers 1997, Lappi and Alén 2011). Prior to the first distillation process the crude tall oil is concentrated by the evaporation of water and other volatile compounds as "heads." The initial concentration phase also removes non-volatile components as tall oil pitch (Wansbrough, Huibers 1997, Aro and Fatehi 2017, Vevere et al. 2020).

Following the initial purification of crude tall oil in the evaporation stage, the crude tall oil mixture undergoes the first distillation process, which separates the more volatile fatty acid components from the rosin acids (Wansbrough, Huibers 1997, Aro and Fatehi 2017, Vevere et al. 2020). The isolated fatty acids undergo a second distillation to remove any remaining volatile compounds, which are combined with the earlier head compounds. The final distillation isolates tall oil fatty acids as the volatile component, from the less volatile distilled tall oil, which contains a mixture of fatty and rosin acids (Wansbrough, Huibers 1997, Aro and Fatehi 2017, Vevere et al. 2020). The combined distillation processes remove the least volatile rosin acids and the most volatile fatty acids in crude tall oil from the final distilled tall oil mixture. The evaporation and subsequent distillations also reduce the number of neutral compounds found in distilled tall oil compared to crude tall oil (Wansbrough, Huibers 1997).

<u>Evaluation Question #3:</u> Discuss whether the petitioned substance is formulated or manufactured by a chemical process, or created by naturally occurring biological processes (7 U.S.C. § 6502 (21)).

As described in Evaluation Question 2, distilled tall oil is a synthetic substance isolated from black liquor as a by-product of the Kraft pulping process, and refined through additional chemical and physical methods. Some of the compounds in distilled tall oil exist naturally in trees, while others are produced in the pulping and refining processes due to their highly alkaline or acidic conditions (Vevere et al. 2020, EPA 2021). The distillation process isolates a mixture of rosin and fatty acids in distilled tall oil based on their physical properties (e.g., vapor pressure, boiling point, solubility). During the distillation processes, volatile and nonvolatile organic compounds, water, salts, and neutrals are removed from the final mixture (Huibers 1997, USDA 2010, Aro and Fatehi 2017, Vevere et al. 2020, EPA 2021).

<u>Evaluation Question #4:</u> Describe the persistence or concentration of the petitioned substance and/or its by-products in the environment (7 U.S.C. § 6518 (m) (2)).

At the time of this report, the author did not find environmental studies on distilled tall oil. 60 – 73.2% of distilled tall oil degrades in environmental conditions over a period of 28 days (WR 2015, IC 2019). The environmental degradation products of distilled tall oil are not specified. Fatty acids are metabolized by many organisms to a host of organic molecules, including sugars, carbohydrates, and ketones (Timberlake 2016). Health Canada has stated that "most components of CTO [crude tall oil] are moderately persistent in water and are expected to be moderately to highly persistent in sediments" (HC 2019). Since distilled tall oil is expected to remain in the soil until it is metabolized by microorganisms, it is likely to react with basic compounds, as described by Equation 1 in the "Action of the Substance" section.

Due to limited data on distilled tall oil, the major components of distilled tall oil, fatty acids and rosin acids were considered. However, the environmental data on these classes of compounds are also limited (EPA 2002, EPA 2005). Using structure activity relationships, the EPA has stated it expects both fatty and rosin acids to pose little risk to leach into water systems, which correlates to the reported water insolubility of distilled tall oil (see Table 4 in "Properties of the Substance") (EPA 2002, 2005). Due to their low water solubility, both fatty and rosin acids are expected to remain in soil and sediment and have the potential to bioaccumulate in soil systems (EPA 2002, EPA 2005).

Fatty acids are common organic and biological classes of compounds and are metabolized by microbes and mammals (EPA 2002, Brogán et al. 2006, Timberlake 2016). Microbial biodegradation of the fatty acids in distilled tall oil is expected to be the primary means of dissipation in the environment, although no environmental half-life was reported (EPA 2002, Brogán et al. 2006). Less is known about the environmental persistence of rosin acids, although the EPA has stated that they are unlikely to be readily biodegradable based on the increased stability of their cyclic structures (EPA 2005). The EPA has estimated that rosin acids may have an environmental half-life that may exceed weeks for primary degradation (EPA 2005).

<u>Evaluation Question #5:</u> Describe the toxicity and mode of action of the substance and of its breakdown products and any contaminants. Describe the persistence and areas of concentration in the environment of the substance and its breakdown products (7 U.S.C. § 6518 (m) (2)).

At the time of this report, the author did not find environmental studies on distilled tall oil. As described in the "Specific Uses of the Substance" and the "Action of the Substance" sections, distilled tall oil has been reported to have insecticidal activity specific to soft-bodied organisms. The insecticidal properties of distilled tall oil may be due to both physical and chemical mechanisms (Cousin 1987, Xie and Isman 1995, Brogán et al. 2006, USDA 2019, Wan and Wang 2020). The primary mode of action for the insecticidal activity of distilled tall oil is based on disruptions to cellular membrane structure and function, which interferes with proper respiration and cellular function.

Distilled tall oil is highly toxic to aquatic life, with a LC_{50} = 0.02 – 0.084 ppm for fish (EPA ECOSAR). Fatty acids are classified as having high toxicity to fish, with a LC_{50} = 0.004 – 0.02 ppm (EPA 2002). Rosin acids have a similar toxicity profile, with acute toxicity to fish, with a LC_{50} = 0.02 – 1.1 ppm (Peng and Roberts 2000, EPA 2005). However, the EPA has stated that toxicity assessments "may well exceed the water solubility of these compounds, further reducing potential risks to aquatic organisms" (EPA 2002, EPA 2005). Distilled tall oil and its components are nontoxic to terrestrial animals, other than soft-bodied insects discussed above (EPA ECOSAR, EPA 2002, EPA 2005, Brogán et al. 2006, ECHA2021, EPA 2021).

As described in Evaluation Question 4, little is known about the degradation of distilled tall oil or rosin acids. Fatty acids are degraded by microbes in the environment. Fatty acids are metabolized to the biomolecule acetyl coenzyme A (acetyl CoA) which is used in the synthesis of many biomolecules including sugars, carbohydrates, and ketones (Timberlake 2016).

Evaluation Question #6: Describe any environmental contamination that could result from the petitioned substance's manufacture, use, misuse, or disposal (7 U.S.C. § 6518 (m) (3)).

As discussed in Evaluation Questions 4 and 5, distilled tall oil is toxic to fish, but is unlikely to leach into water systems due to its hydrophobic nature. Additionally, distilled tall oil has a low toxicity to terrestrial organisms, with the exception of soft-bodied insects in some pesticide formulations. These considerations make distilled tall oil unlikely to contaminate the environment if used as petitioned. However, the substance could be hazardous to aquatic life if misused or improperly disposed of by applying or discharging to water systems (EPA ECOSAR, Peng and Roberts 2000, EPA 2002, EPA 2005).

Distilled tall oil is a byproduct of the paper industry. Environmental contamination and degradation is possible in the logging of forests required to produce distilled tall oil and other products derived from the Kraft process. Forests are important in fighting climate change through natural carbon sequestration, stabilizes soil and watershed systems, and provide habitat for biological diversity (Rex 2003, EPA 2017b, WWF 2021). In addition to the loss of carbon sequestration, deforestation contributes to 15% of global greenhouse emissions (WWF 2021).

Environmental contamination is possible during the production of distilled tall oil. The use of highly corrosive concentrated sulfuric acid in the acidulation process presents a potential source of environmental contamination. However, the neutralization of the acid in the acidulation process reduces the acidity of the resulting solution. Additionally, the recycling of the spent acid, as discussed in Evaluation Question 2, further mitigates the risk associated with the sulfuric acid and further neutralizes the acidic solution.

Sulfide ions from mercaptans and other compounds react with sulfuric acid, producing hydrogen sulfide gas (H_2S) during the acidulation process, as shown below in Equation 5 (Wansbrough, Aro and Fatehi 2017). Hydrogen sulfide is a toxic gas that must be removed from the production stream through gas scrubbers (Wansbrough, Silberberg 2003, Aro and Fatehi 2017). Current production facilities capture and neutralize all the hydrogen sulfide generated, although its generation in the production process gives the potential for unintended release (Wansbrough, Aro and Fatehi 2017).

$$H_2SO_{4\,(aq)} + S^{2-}{}_{(aq)} \rightarrow H_2S_{(g)} + SO_4^{2-}{}_{(aq)}$$

Equation 5

Evaluation Question #7: Describe any known chemical interactions between the petitioned substance and other substances used in organic crop or livestock production or handling. Describe any environmental or human health effects from these chemical interactions (7 U.S.C. § 6518 (m) (1)).

As discussed in Evaluation Questions 4-6, distilled tall oil has the possibility to accumulate in soils, although it is not expected to leach into water systems or pose a risk to non-target terrestrial organisms. As described above in "Composition of the Substance," distilled tall oil is made up of weak organic acids. Since distilled tall oil is expected to remain in the soil until it is metabolized by microorganisms, it is likely to react with basic compounds, as described by Equation 1 in the "Action of the Substance" section. The acidic nature and relatively long lifetime of distilled tall oil may result in the acidification of the soil system. Distilled tall oil may also react with basic compounds used in agricultural production, including soil pH adjusters such as calcium carbonate (limestone) and lime, and soil amendments, including ash and biochar (NOP 2016).

The organic acids present in distilled tall oil have the potential to chelate micronutrient metal species, as described in Equation 2 in the "Action of the Substance" section. As described earlier in "Action of the Substance," the chelation of metal micronutrients will prevent them from leaching into water systems by increasing their hydrophobic character. However, the chelation and increased hydrophobicity of the micronutrient may also reduce its bioavailability in the soil system. Distilled tall oil may interact with several metal cations (e.g., calcium [Ca^{2+}], iron [$Fe^{2+/3+}$], copper [$Cu^{+/2+}$], magnesium [Mg^{2+}], etc.), which may impact approved salts outlined in 7 CFR 205.601.

Additionally, the reaction of an acidic compound with a base in the environment, as described in Equation 1, will generate a tall oil soap. The ionic nature of tall oil soap will result in increased water solubility, although the degree of improved solubility is also dependent on the corresponding cation, which is dictated by the base (Equation 1) (Silberberg 2003, Shriver and Atkins 2008, Timberlake 2016). Despite the ionic nature of a tall oil soap, the substance is still likely to have limited water solubility due to the large proportion of nonpolar hydrocarbons that make up distilled tall oil compounds (USDA 2020b).

Evaluation Question #8: Describe any effects of the petitioned substance on biological or chemical interactions in the agro-ecosystem, including physiological effects on soil organisms (including the salt index and solubility of the soil), crops, and livestock (7 U.S.C. § 6518 (m) (5)).

As discussed in Evaluation Questions 4-7, distilled tall oil is likely to remain in the soil system until it undergoes metabolism by microorganisms. As discussed in Evaluation Question 7, distilled tall oil has the potential to react with basic compounds in the soil and lower the soil pH (Equation 1). Additionally, the tall oil soaps that would be generated when distilled tall oil compounds are neutralized by environmental bases are likely to moderately increase their water solubility and have the potential to interact with metal micronutrients via chelation (Equation 2).

According to the EPA Ecological Structure-Activity Relationship Model (ECOSAR), distilled tall oil is moderately toxic to earthworms, with a LC_{50} = 140 ppm (EPA ECOSAR). As discussed in Evaluation Questions 4 and 5, there is little environmental data on the action of distilled tall oil, although it is expected to be unlikely to harm non-target terrestrial organisms (EPA 2002, EPA 2005, ECHA 2021). The available EPA and ECHA reports do not provide information on the impact of distilled tall oil on the solubility or salt index of soil systems.

Evaluation Question #9: Discuss and summarize findings on whether the use of the petitioned substance may be harmful to the environment (7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i)).

As discussed in Evaluation Questions 4-8, distilled tall oil has relatively unknown environmental lifetimes, with rosin acids expected to be longer lived than fatty acids. The environmental half-life of distilled tall oil is predicted to be on the order of weeks or longer (EPA 2002, EPA 2005). Distilled tall oil is expected to undergo eventual metabolism by soil microorganisms.

As discussed in Evaluation Questions 5, 6, and 8, distilled tall oil is toxic to fish, although it is not expected to leach into water systems because of its hydrophobic character. Distilled tall oil is moderately toxic to earthworms but is not expected to be toxic to other non-target terrestrial organisms.

<u>Evaluation Question #10:</u> Describe and summarize any reported effects upon human health from use of the petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (i), 7 U.S.C. § 6517 (c) (2) (A) (i)) and 7 U.S.C. § 6518 (m) (4)).

Distilled tall oil has low human toxicity, with a LD_{50} = 6000 mg/kg (body weight), no observable effects level (NOEL) of 80 mg/kg (body weight)/day, and lowest observable adverse effects level (LOAEL) of 414 mg/kg (body weight)/day (USDA 2010). Distilled tall oil may cause skin and eye irritation (WR 2015).

Rosin acids have low toxicity in humans and other mammals, with LD_{50} values ranging from 4600 – 7600 mg/kg (body weight)/day for mice, rats, and guinea pigs (EPA 2005). Studies have shown that diets high in rosin acids (1.0%) decreased organ and body weight in rats, although no toxicity or increased mortality was noted (EPA 2005). Rosin acids are expected to have low human toxicity due to their poor absorption (EPA 2005).

Fatty acids are a key part of the human diet in the United States, making up 20 – 60% of daily diet (EPA 2002, Timberlake 2016). Fatty acids are metabolized to the biomolecule acetyl coenzyme A (acetyl CoA) which is used in the synthesis of many biomolecules including sugars, carbohydrates, and ketones (Timberlake 2016).

<u>Evaluation Question #11:</u> Describe all natural (non-synthetic) substances or products which may be used in place of a petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (ii)). Provide a list of allowed substances that may be used in place of the petitioned substance (7 U.S.C. § 6518 (m) (6)).

Alternative nonsynthetic sources of fatty acids, as an alternative to those in distilled tall oil, include vegetable oil, soybean oil, canola oil, corn oil, cottonseed oil, fish oil, jojoba oil, neem oil, and sesame oil (USDA 2010, NOP 2016, USDA 2019, Wan and Wang 2020). The similar chemical composition of these substances to one of the major class of compounds in distilled tall oil would result in similar solution polarity and surfactant properties. These compounds are likely to provide for similar sticker, anti-leaching, and time release characteristics as distilled tall oil. However, these substances are unlikely to have the same viscosity as distilled tall oil due to the absence of more viscous rosin acids.

Other natural oils provide similar hydrophobic properties to distilled tall oil and the alternative nonsynthetic sources listed above, including anise oil, citronella oil, clove oil, bergamot oil, linseed oil, lemongrass oil, mint oil, and thyme oil (NOP 5034-1). Additionally, the narrow-range dormant, suffocating, and summer oils offer nonpolar synthetic alternatives that have been approved for organic use in 7 CFR 205.601 (USDA 2019). These compounds are likely to solubilize nonpolar compounds, although they are unlikely to solubilize the same range of compounds as distilled tall oil due to the absence of carboxylic acid groups. The nonpolar nature of these compounds is also likely to provide similar action as stickers, anti-leaching, and time release agents. These substances are unlikely to have the same viscosity as distilled tall oil due to the absence of more viscous rosin acids.

Pine rosins provide a nonsynthetic source of rosin acids (NOP 5034-1). Like the natural sources of fatty acids listed above, pine rosins provide a chemical composition similar to one of the major classes of compounds in distilled tall oil and are likely to provide similar solution polarity and surfactant properties. These compounds are likely to provide for similar sticker, anti-leaching, and time release characteristics as distilled tall oil. However, these substances are unlikely to have the same viscosity as distilled tall oil due to the absence of less viscous fatty acids.

A natural alternative to distilled tall oil may be created by the combination of natural fatty acids with natural rosin acids. These substances could be mixed at differing ratios to provide optimal solvent properties for each specific application. Natural gums may also be added to natural fatty acids and both natural and synthetic oils to adjust viscosity. Gums offer viscous mixtures of polysaccharides that may serve as thickeners (NOP 5034-1, USDA 2018). Additionally, the increased polarity of these mixtures could be used to adjust solvent properties based on individual applications (Timberlake 2016).

Evaluation Question #12: Describe any alternative practices that would make the use of the petitioned substance unnecessary (7 U.S.C. § 6518 (m) (6)).

There are a variety of alternative practices that would make the use of distilled tall oil unnecessary, such as the adoption of physical nets and barriers to protect from insect infestation. Nets and other physical barriers are effective against pests such as beetles and leafminers without any negative environmental effects (Southside 2009, Rebek and Hillock 2016). However, physical barriers are not effective against all insects, and may not be applicable to all settings and types of crops. Additionally, nets may be costly, making such methods impractical and difficult to scale up in large agricultural settings.

In some cases, mechanical removal of insects is a possible alternative to pesticides. Mechanical removal can take many forms including by hand, agricultural tools (e.g., skewers, etc.), and water streams (Southside 2009, Muntz et al. 2016, Rebek and Hillock 2016). This is a desirable alternative due to the lack of environmental consequences and low technology requirements. Mechanical removal is also more effective against larger insects, such as beetles, hornworms, and cutworms (Southside 2009). However, this alternative is not suited to all agricultural applications. Manual removal can be time consuming, labor-intensive and expensive, making it difficult to scale up to large agricultural applications.

Insects can also be reduced by agro-ecosystem management designed to prevent the growth of insect populations by weeding, crop irrigation, fertilization, or mulching. Such approaches produce more robust crops that are better suited to withstand pest infestations (Southside 2009, Muntz et al. 2016, Rebek and Hillock 2016). The removal of weeds eliminates a potential habitat to harbor pest communities. Crop rotation and seasonal planting contribute to more robust plants by fostering healthy soil systems (Muntz et al. 2016). Seasonal crop planting can also prevent pest infestations by strategically planting crops that are most resistant to seasonal pest populations (Muntz et al. 2016, Rebek and Hillock 2016).

There are also alternatives to the anti-leaching and time release applications of distilled tall oil. Alternatives include the adoption of soil amendments, utilizing ash, biochar, humates, clay, or lignin sulfonate (NOP 2016). These substances improve the holding capacity of nutrients and other agricultural formulations due to their abilities to act as natural chelates, thereby preventing pesticides, fertilizers, and micronutrients from leaching into water systems (USDA 2012, USDA 2020c).

Report Authorship

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