United States Department of Agriculture
Agricultural Marketing Service | National Organic Program
Document Cover Sheet
https://www.ams.usda.gov/rules-regulations/organic/national-list/petitioned

Document Type:

☒ **National List Petition or Petition Update**

A petition is a request to amend the USDA National Organic Program's National List of Allowed and Prohibited Substances (National List).

Any person may submit a petition to have a substance evaluated by the National Organic Standards Board (7 CFR 205.607(a)).

Guidelines for submitting a petition are available in the NOP Handbook as NOP 3011, National List Petition Guidelines.

Petitions are posted for the public on the NOP website for Petitioned Substances.

☐ **Technical Report**

A technical report is developed in response to a petition to amend the National List. Reports are also developed to assist in the review of substances that are already on the National List.

Technical reports are completed by third-party contractors and are available to the public on the NOP website for Petitioned Substances.

Contractor names and dates completed are available in the report.

legnochem

July 29, 2019

National List Manager
USDA/AMS/NOP,
Standards Division
1400 Independence Ave.
SW Room 2648-So.,Ag Stop 0268
Washington, DC 20250-0268

Please find attached a revised petition to have sodium carbonate lignin added to §205.601 (j)(4) of the National List as another form of lignin along with lignin sulfonate, a synthetic substance for use as a plant or soil amendment, as a dust suppressant.

This petition replaces the petition for sodium carbonate lignin submitted July 8, 2019 which requested an annotation change. As part of the review process and discussions with Devon Pattillo, Agricultural Marketing Specialist, it was decided based on the information we presented, that rather than request an annotation change, we present sodium carbonate lignin as a new substance equivalent to lignin sulfonates.

The most recent sunset review for lignin sulfonate demonstrated substantial support for lignin compounds as a dust suppressant in plant and soil amendments and it received relisting on the National List until 2022 as a chelation agent and dust suppressant. We present in this petition the grounds for considering sodium carbonate lignin as another form of lignin, equivalent to lignin sulfonates and demonstrate the flaws in the existing annotations in that they are unnecessarily restrictive and misrepresentative of the true nature of lignin compounds.

Respectfully,

Denis Major
Legnochem
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Sturgeon Falls,Ontario
Canada, P2B 0B3

Petition Prepared By:

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Item A.1— Indicate which section or sections the petitioned substance will be included on and/or removed from the National List.

This petition seeks to add Sodium Carbonate Lignin or Sodium Lignin (names used interchangeably) to 7 CFR§205.601(j)(4) as a synthetic substance allowed for use in organic crop production as a plant and soil amendment for dust suppression in addition to lignin sulfonate.

Currently 7 CFR§205.601(j)(4) states "Lignin sulfonate—chelating agent, dust suppressant".

We wish it to be amended to state: "Lignins and lignin sulfonates (lignonsulphonates) – chelating agent, dust suppressant"
IF the intention is to continue to *implicitly* permit the salts of lignin sulfonates and thus sodium carbonate lignin without naming them specifically.

Note that lignin sulfonate and lignosulphonates are considered the same and used interchangeably.

It would be clearer however to state the compounds of lignin and lignin sulfonates that are currently permitted and to be permitted.
In this case 7 CFR§205.601(j)(4) would be amended to state:
"Lignins and lignin sulfonates – chelating agent, dust suppressant. Other lignin forms such as lignosulfonic acid, calcium lignosulfonate, magnesium lignosulfonate, sodium lignosulfonate and sodium carbonate lignin are permitted. Ammonium lignosulfonate is permitted with restrictions."

Materials review agencies such as OMRI do not have the authority to make interpretations on substances outside of what is named in CFR§205.601 and so naming the forms of lignin that are permitted would provide much needed clarity. The OMRI generic materials list currently includes the following lignin sulfonate salts as allowable inputs to organic production: sodium lignosulfonate, magnesium lignosulfonate, ammonium lignosulfonate, and calcium lignosulfonate (OMRI, 2018). Yet these lignosulfonate salts are not specifically identified on the National List.

Item A.2 — OFPA Category - Crop and Livestock Materials:

This petition applies to the OFPA category of Crop Production aids.

Item B—
Provide concise and comprehensive responses in providing all of the following information on the substance being petitioned. For petitions to add or change an annotation for a substance that is already on the National List, items 5-11 are optional. Petitioners are encouraged to address these items if the information has changed since the NOSB's original review of the substance.

1. Substance Name :
Provide the substance's chemical and/or material common name. The name of the petitioned substance should be consistent with any name(s) used by other Federal agencies (e.g., FDA, EPA, etc.)

The substance name is Sodium Carbonate Lignin also commonly known as Sodium Lignin. Other common names are Polybond, Polybind, Soda Lignin, black liquor of soda pulping, spent liquor of soda pulping.

Please note that because lignin is bound to cellulose in plants, some form of extraction technology is necessary to access it. As a result the mixture of lignin compounds have been named based on the cooking chemicals or process used for delignification. While attempts have been made to standardize the nomenclature there is confusion in naming identification and CAS numbering.

2. Petitioner and Manufacturer Information:
Provide the name, address, and telephone number for the petitioner and manufacturer (if different).

Petitioner:
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Example Manufacturers:
Sonoco Products Company
1 North 2nd St.
Hartsville, South Carolina
USA 29550

Cascades Inc.- Trenton
300 Marmora Street
Trenton, Ontario
Canada K8V 5R8

3. Intended or Current Use:
Describe the intended or current use of the substance, e.g., use as a pesticide, animal feed additive, processing aid, non-agricultural ingredient, sanitizer, or disinfectant. If the substance is an agricultural ingredient, the petition must provide a list of the types of product(s) (e.g., cereals, salad dressings) for which the substance will be used and a description of the substance's function in the product(s) (e.g., ingredient, flavoring agent, emulsifier, processing aid).

The intention is to use sodium carbonate lignin as a binder for the pelletization of mined minerals used as soil amendments for organic production in order to supress dust (particulate matter) during spreading and handling. The active ingredient is lignin complexed with hemicellulose which acts as a dust suppressant due to its large size and affinity for binding with other polar and nonpolar compounds. The smaller dust compounds adsorb to the lignin compound and form a larger, heavier complex that is not as friable, and suppresses dust (CWPA, 2005).

Another common application of sodium carbonate lignin as a dust suppressant is for unpaved roads and other surfaces. This application is not for crop production and thus is not addressed in this petition.

This petition does not address sodium carbonate lignin's potential use as a chelation agent although it is currently used in conventional farming for this purpose and is recognized as an effective chelation agent.

Lignin sulfonate is currently allowed as a dust suppressant and chelation agent under 7 CFR§205.601(j)(4) for the same purposes. This petition asserts that sodium carbonate lignin is an equivalent and benign form of lignin with comparable binding qualities to lignin sulfonate. In terms of binding qualities, the sulfonation of lignin is not relevant and we maintain that the original intent and criteria for acceptance of lignin sulfonate as an allowable synthetic for crop production also applies to sodium carbonate lignin. The basis for equivalency is provided in section 13 Petition Justification Statement.

4. Intended Activities and Application Rate:

Provide a list of the crop, livestock, or handling activities for which the substance will be used. If used for crops or livestock, the substance's rate and method of application must be described.

Sodium carbonate lignin is intended to be used as a binding agent to granulate minerals (primarily lime, gypsum and rock phosphate) to virtually eliminate dust during broadcasting and handling. These minerals are commonly used to adjust pH and as supplements to balanced organic soil building programs for a full range of possible plants and crops.

As a binding agent for minerals, sodium carbonate lignin is added at a rate of 1-5% of weight of binder solids (in a solution) to dry weight of mineral processed with 2% being the standard practice.

Pelleted minerals are then applied to soils or growing medium at rates set out by soil test results specific to each application. Field application is primarily done using mechanical type spreaders. These include conventional rotary broadcasting spreaders and trough-type spreading devices.

Table 1 below identifies minerals normally granularized with lignin compounds and the typical application rates for plant and crop production.
Table 1:

Mineral	Use	Application rate
Lime	To raise PH	0.25 – 4 Tonne/ac 1- 2 Ton/ac typical
Lime	To increase calcium as nutrient source	100-300 lb/ac
Gypsum	Improve clay soil structure	Up to 2 Ton/ac
Gypsum	Correct sodic soils Turf and plant soil	0.5 to 4 T/ac

	conditioner	
Gypsum	To add Sulphate as nutrient source	50-250 lb/ac
Rock Phosphate	To increase phosphate (K) as nutrient	50- 500lb/ac

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

Manufacture of Sodium Carbonate Lignin:

Sodium carbonate lignin is a co-product derived from the soda wood pulping process. It is in the first stage of the pulping process in which lignin and hemicellulose are separated from cellulose fiber for the production of pulp.

There are two basic soda ash (sodium carbonate, Na_2CO_3) pulping processes. The first uses only sodium carbonate as active pulping agent and the other uses differing combinations of sodium carbonate and caustic soda (sodium hydroxide, NaOH). Owens Illinois was granted a US patent which covers pulping of hardwood from about 15% to 50% of the total chemical as NaOH and 50% to 85% of chemical as Na_2CO_3, both expressed as sodium oxide (Na_2O).

In the first instance the sodium carbonate lignin is produced by cooking wood chips in steam at a pressure of 1100 kPa in the presence of mild solution of Na_2CO_3 (at 115 g/L or 6-8% solution) for about 14 minutes. As a result, the wood chips are softened so that they can subsequently be separated into individual fibres during the refining stage. The wood chips are then compressed mechanically to separate the spent sodium carbonate and lignin liquor from the wood chips.

The other modified soda ash processes may use a 15-50% of total chemical as NaOH as make up along with the Na_2CO_3 (Yayin, Irmak,1992).

The spent sodium carbonate lignin liquor that has been separated is next evaporated to produce a solution of 45-55% solids liquor, or a dry powder, which comprises the final substance and the subject of this petition.

The soda process is often referred to as 'semi-chemical pulping' when compared to other pulping processes as it is much simpler (less process steps) and does not use any sulphur or bleaching chemicals.

The resulting lignin liquor contains lignin fragments, carbohydrates from the breakdown of hemicellulose and residual sodium carbonate. Lignin is at different levels of degradation and complexing with hemicellulose and cellulose in this mixture.

The primary use of the pulp produced from soda pulping is for natural (unbleached) corrugated (fluting) material and is considered more environmentally friendly than sulfate processes used for higher grade paper production. (EPA 2017 Chemical Wood Pulping)

Of note is that the soda pulping process represents only approximately 4% of pulping methods worldwide and due to its minor production, was not considered as a source of lignin when lignin sulfonates were reviewed by the NOP in the past. It can be shown that the lignin fragments and sodium carbonate produced by the soda process are in fact also present in the lignin sulfonate liquors (Kraft lignin, sodium lignosulfonate) already accepted by the NOSB. This information is confirmed in the technical review by Khalil Jradi Appendix C.

How Sodium Carbonate Lignin is used for pelletization/ granularization:

Binder solution is applied to a finely ground mineral as it moves across a conveyer in a finely atomized mist at a set ratio. The mixture then moves to a mixer trough which blends the binder solution with the mineral and also pre-agglomerates the mineral into very tiny "seed" pellets. Different minerals will require different moisture levels to pelletize due to fineness and differing amounts of constituents. Moisture levels usually range between 8% and 14%, 10% being most common. The greatest portion of binder solution is applied at the mixer, 90% or more of the total sum.
The conditioned and "seeded" mineral is next conveyed to a disc pelletizer where it is introduced to a rotating pan. The rotating pan of the disc pelletizer continues to agglomerate the mineral into larger pellets. The rotating pan causes the pellets to cascade off of it. The cascading bed of pellets, because of the angle of inclination, acts to classify the product spilling over the lip of the pan. The result is a very uniformly sized pellet. A small amount of binder solution, usually less than 10% of the total, is applied in a fine spray at the disc pelletizer.
Overall, Sodium Carbonate Lignin is added at a rate of 1-5% of weight of binder solids (in a solution) to dry weight of mineral processed with 2% being predominantly the standard practice.

The wet pellets are then dried using passive air drying or heaters and graded according to size. (IBA 2001 Veverka, Hinkle)

6. Ancillary Substances:

For substances petitioned for use in organic handling or processing, provide information about the ancillary substances (including, but not limited to, carriers, emulsifiers, or stabilizers) that may be included with the petitioned substance, including function, type of substance, and source, if known.

There are no ancillary substances included with the petitioned substance.

7. Previous Reviews:

Provide a summary of any available previous reviews of the petitioned substance by State or private certification programs or other organizations. If this information is not available, this should be stated in the petition. If the substance has been previously reviewed and rejected by the NOSB, the petition must provide new information that was not submitted in an earlier petition or provided for in the previous technical reports for the substance.

There were no previous reviews by the NOSB or other private certification programs found for lignin produced from the soda ash process or 'sodium carbonate lignin' specifically.

OMRI has previously reviewed sodium lignin and although it was agreed that it has merit to be considered an equivalent substance to lignin sulfonates, OMRI judged that they cannot accept it unless it is specifically named on the National List or there is a technical guidance issued by the NOP. OMRI identified that they do not have the jurisdiction to make technical assessments or interpretations outside of what is specifically named on the list. Following this determination, a request was sent to Dr. C. Mathews the National List manager to determine if a guidance could be issued on the subject by the NOP. We are awaiting a decision on this matter but decided to proceed with a new petition given Dr. Mathews is no longer the National list manager.

However, lignin sulfonate, another form of lignin intended for the same purposes, has been reviewed a number of times and is relevant to this petition on the basis that sodium carbonate lignin and lignin sulfonate are essentially equivalent substances. There are two grounds for this assertion:

First, that lignins extracted from pulping are very broadly named and defined and second, that the beneficial active ingredient is natural lignin complexed with cellulose and hemi-cellulose which is present in many forms in these extractions. We assert that the compounds found in sodium carbonate lignin liquor are also found in lignin sulfonate liquors, making them essentially equivalent compounds with comparable binding qualities and impacts.

We have presented the evidence and basis for this equivalency in section 13: Petition Justification Statement.

Based on this assertion, the history on lignin sulfonate reviews is therefore presented here:

Lignin sulfonate is currently included on the National List as a synthetic substance allowed for use in organic production (7 CFR 205.601). Lignin sulfonate may be used in organic crop production as a plant or soil amendment as a dust suppressant or chelating agent 205.601(j)(4) and until 2015 as a flotation agent in post-harvest handling under 205.601(l).

In 2015 Lignin Sulfonate was reviewed by the NOSB for its use as a flotation agent for fruit in postharvest handling and a motion to have it removed from 205.601 (l) was carried.
At the same 2015 board meeting, Lignin Sulfonate was relisted until the next sunset date of 2022 in 205.601(j)(4) as plant or soil amendments with the annotations: chelating agent, dust suppressant. Please reference the NOSB Technical Evaluation Report prepared in 2013 (Appendix B) and the 2017 NOSB final review regarding its Sunset relisting.

Lignin sulfonate is also currently under review by the NOSB for use in organic aquatic animal production, specifically a non-nutritive feed binder for use in aquaculture. A NOSB Technical Review 2013 (Appendix B) and a favorable 2014 livestock subcommittee report have been completed but the petition is still under review for final board approval.

Calcium lignosulfonate (CAS No. 8061-52-7) and sodium lignosulfonate (CAS No. 8061-51-6) may be used as inert ingredients in pesticide products. These inert ingredients are on EPA's inert ingredients list (List 4B) which, in combination with List 4A, was used as a reference for allowed inert ingredients in organic pesticide products.

Several international organic organizations allow the use of lignin sulfonate in organic food production. The Canadian General Standards Board allows the use of lignin sulfonate as a dust suppressant, formulant ingredient, and chelating agent (CGSB amended 2018. Can/CGSB-32.311-2015 Permitted Substances List). The Canadian General Standards Board has revision requests to Can 32.311 Permitted Substances List before it as of this writing, 'to allow other forms of lignin', including Sodium Carbonate Lignin submitted by Eco-Cert Canada and Legnochem.
The Technical committee has met and as of this writing the proposed revision to the annotation is:

> *Lignin and lignin sulphonates (lignosulphonates)* (the word lignin is added)

> *Ammonium lignosulphonate is prohibited. Other lignin forms such as lignosulphonic acid, calcium lignosulphonate, magnesium lignosulphonate and sodium lignosulphonate are permitted.*
> *Permitted as a chelating agent, as a formulant ingredient and as a dust suppressant.*

The International Federation of Organic Agriculture Movements (IFOAM) includes calcium lignosulfonate on its Indicative List of Substances for Organic Production and Processing. No other lignin sulfonates are included (IFOAM, 2008). As of 2009, calcium lignosulfonate is allowed by the CODEX Alimentarius Commission as a food additive, and the compound has been assigned INS Number 1522 (Codex Alimentarius Commission, 2010). (NOSB 2013 Technical Evaluation Report)

In 2008, the Ministry of Agriculture, Forestry, and Fisheries (MAFF) in Japan lifted an existing ban on lignin sulfonate used as a dust suppressant or chelating agent in organic crop inputs but maintained the ban on lignin sulfonate used in post-harvest handling (i.e. floatation agent for pears and stone fruit). At that time, products exported to Japan were required to have verification that they were handled without lignin sulfonate, be accompanied by an export certificate, and be imported by a JAS- certified importer (USDA, 2009). The restriction on lignin sulfonate as a handling material for organic products exported to Japan was dropped when US/Japan Equivalency Arrangement went into effect. (January 1, 2014). Lignin sulfonate is not specifically discussed by the European Union Regulations. (NOSB 2013 Technical Evaluation Report)

8. Regulatory Authority

Provide information regarding EPA, FDA, and State regulatory authority registrations, including registration numbers. The information provided must confirm that the intended use of the substance is permitted under EPA or FDA regulations, as applicable. For food ingredients and processing aids, the substance must be approved by FDA for the petitioned use. For pesticide active ingredients, the substance must have an EPA tolerance or tolerance exemption, as applicable. If this information does not exist or is not applicable, the petitioner should state this in the petition.

Sodium carbonate lignin is not currently registered under EPA, FDA or other state regulatory registrations. As another form of equivalent lignin, lignin sulfonate's approved legal uses are discussed here. Please reference the NOSB Technical Evaluation Panel Report 2013 in Appendix B.

Lignin sulfonate may be used in organic crop production as a plant or soil amendment (dust suppressant, chelating agent) under7 CFR §205.601(j)(4).

The most recent sunset review for lignin sulfonate demonstrated substantial support for lignin compounds as a dust suppressant in plant and soil amendments and it received relisting on the National List until 2022 as a chelation agent and dust suppressant.

Of great relevance to this petition is that the OMRI generic materials list includes the following lignin sulfonate salts as allowable inputs to organic production: sodium lignosulfonate, magnesium lignosulfonate, ammonium lignosulfonate, and calcium lignosulfonate (OMRI, 2018). These lignosulfonate salts are not specifically identified on the National List.
According to OMRI, ammonium lignosulfonate is an allowed form of lignin sulfonate, with restrictions, for use as a nutrient chelate in organic fertilizer products. According to OMRI, formulated fertilizer products that contain ammonium lignosulfonate may not make nitrogen claims on the label and/or the contribution

of ammonium lignosulfonate to the total nitrogen content of the formulated product must be less than 1% based on 7 CFR 205.601(j)(4), 7 CFR 205.601(l)(1), and OMRI, 2018 .

Under 21 CFR 573.600(a) and (b), the FDA Food Additives Permitted in Feed and Drinking Water of Animals, lignin sulfonate (including the ammonium, calcium, magnesium, or sodium salts of lignin sulfonate) may be used in a liquid form (moisture not to exceed 50% by weight) or a dry form (moisture not to exceed 6% by weight) in animal feeds. As specified at 21 CFR 573.600(b), lignin sulfonate may be used in an amount calculated on a dry weight basis:
(1) As a pelleting aid in the liquid or dry form in an amount not to exceed 4 percent of the finished pellets.
(2) As a binding aid in the liquid form in the flaking of feed grains in an amount not to exceed 4 percent of the flaked grain.
(3) As a surfactant in molasses used in feeds, as a liquid lignin sulfonate, in an amount not to exceed 11 percent of the molasses.
(4) As a source of metabolizable energy, in the liquid or dry form, in an amount not to exceed 4 percent of the finished feed.

Calcium lignosulfonate (CAS No. 8061-52-7) and sodium lignosulfonate (CAS No. 8061-51-6) may be used as inert ingredients in pesticide products. (List 4B -USDA, 2009; U.S. EPA, 2010).

9. Chemical Abstracts Service (CAS) Number and Product Labels:

Provide the CAS number or other product numbers of the substance. If the substance does not have an assigned product number, the petitioner should state so in the petition. For food additives, the International Numbering System (INS) number should also be provided. This item should also include labels of products that contain the petitioned substance. If a product label does not apply to this substance, please provide a brief explanation. Product specification sheets, product data sheets, non-retail labels, or other product information may be substituted for the product label, if appropriate.

Note: This list of CAS numbers serves to illustrate the confusion with naming and identification of lignin liquors. For example, CAS numbers can be found for lignin and lignin sulfonate sometimes with both named under the same number. (Eg. CAS # 8061-05-01 for Lignin, Alkali also lists soda lignin and sulfate lignin, Lignin and Kraft Lignin).

CAS # 37203-80-8: Lignin, sodium salt
CAS # 8068-05-01: Lignin, alkali. - This CAS number is a generic CAS number for lignin's derived from many different wood pulping processes. Lists lignin, Kraft , lignin alkali, soluble lignin, soda lignin, sulfate lignin, sulphate lignin etc..
CAS # 68201-23-0: Lignin alkali carboxylated, Lignin, oxidized pine lignin. other names: Lignin alkali oxidized sodium salt
CAS# 68512-36-7: Lignin, alkali, oxidized
CAS # 68201-23-0: lignin, alkali, carboxylated
CAs # 8061-51-6: lignosulfonic acid, sodium salt synonyms- lignosulfonic acid, sodium salt, desulfinated spent pulping liquor, sodium base spent sulfite liquor, sulfonated lignin sodium salt, etc.

Because this product is normally sold in bulk, package labels are not available. In order to satisfy the requirement for a label of products that contain the substance, two MSDS are provided for pelleted product. One is for Castle Pelletized Lime and the other is for Baker Lime pelletized lime. A third label is provided for sodium carbonate lignin used to pelletize animal feed.

10. Physical and Chemical Properties:

Note: Appendix C is a technical review by Khalil Jradi PhD chemistry, a subject expert on lignin and pulp liquors. The study was commissioned to support the physical and chemical information given in this document and to validate the assertion that sodium lignin and lignin sulfonates are essentially equivalent compounds.

General composition of the lignin liquor:

Lignin exists naturally in all woody plants as a structural and strengthening component. Because lignin is integrated into the plant cell wall, there are no natural processes that liberate lignin other than natural decomposition of wood by microorganisms. As said previously, some form of extraction is necessary to access it.

Lignin, produced from the sodium carbonate pulping process, as described in the response to Question #5, is removed from the wood chips using heat in the presence of a solution of only sodium carbonate (Na_2CO_3) or a mixture of sodium carbonate and sodium hydroxide (NaOH) in water. The spent chemical solution (liquor) is then mechanically separated from the wood fiber after extraction. During this process, hydroxyl ions in solution catalyze the hydrolysis of ether and ester bonds between cellulose and lignin, releasing free lignin and lignin complexed with hemicellulose. (Yayin, Irmak, 1992).

The resulting liquor is a heterogeneous mixture of lignin fragments, carbohydrates from the breakdown of hemicellulose and cellulose, and the residual sodium carbonate. Lignin (and hemicellulose) extracted using the sodium carbonate pulping process is considered to be very close to its natural state.

Residual Sodium Carbonate in Liquor:

The main inorganic components of sodium carbonate liquor are Na_2CO_3, NaOH, and metal elements (principally Na, Zn, Mn, K, and other metals in the trace level).

Sodium carbonate and sodium hydroxide in solution with lignin are very benign. Sodium carbonate is mined in several areas of the US, which provides nearly all the domestic consumption. It is well known domestically for its everyday use as a water softener. Sodium Carbonate has an FDA rating of GRAS (generally regarded as safe) and is not classified by EPA as an inert of toxicological concern. CFIA lists it as a permitted food additive.

Sodium carbonate is allowed on the national list in 7 CFR §205.605 (a) Non-agricultural (nonorganic) substances allowed as ingredients in or on processed products labeled as “organic” or “made with organic (specified ingredients or food group(s)).”

Sodium hydroxide is also used in water treatment to control acidity and is used widely in medicinal and cosmetic products. The Food and Drug Administration (FDA) allows sodium hydroxide as a food additive at levels lower than 1 percent.

Physical Property Table For Sodium Carbonate Lignin Liquor at 50% solids:

Chemical or Physical Property	Value
Color	Dark brown liquid
Physical State	Viscous Liquid
Odor	Wood odor
Melting Point Deg C	-8 Deg C
Boiling Point	100 Deg C

Solubility	Completely soluble
Stability	Very stable
Reactivity	Reacts mildly with acids due to small proportion of sodium carbonate, producing carbon dioxide. Mildly reactive to metals.
Oxidizing or Reduction Action	Reacts as mild base to neutralized bases. Usually does not react as reducing or oxidizing agent.
Flammability/ Flame Extension	Flash point data not available although probably combustible.
Explodability	Not available
PH	6.0 – 9.0 (7.0-9.0 being most common)

Mode of Action as Dust Suppressant:
The primary mode of action of sodium carbonate lignin is in binding smaller dust compounds by adsorbing them to the lignin compound and forming larger heavier complexes that are not so friable.

(a) Chemical interactions with other substances, especially substances used in organic production;

A stipulation for the use of mined minerals for organic production is that a mineral must not have undergone any change in its molecular structure through heating or combining with another substance. Based on sodium carbonate lignin's intended use as a binder for the pelletization of mined minerals (dust suppressant), chemical interactions with soil and minerals such as lime, gypsum and rock phosphate are not expected. Instead, when lignins come into contact with small elemental particles through their use as binder/dust suppressants, the soil particles are adsorbed to the lignin complex due to the presence of polar and non-polar areas on the surface of the lignin molecule. These interactions do not result in chemical change but are mostly limited to a physical binding and adsorption. (CWPA 2005, Khalil Jradi Appendix C)

Based on the type of interaction we can conclude that sodium carbonate lignin does not change the molecular structure of the minerals being pelletized during addition, mixing and drying making sodium carbonate lignin an acceptable binder for minerals.

(b) Toxicity and environmental persistence;

Sodium carbonate lignin itself is generally considered to be of relatively low toxicity, except at high doses.

Lignin derivatives discharged into water bodies from open systems may cause foaming and discoloration. Due to their high biological oxygen demand (BOD) during breakdown in water, lignin compounds such as lignosulfonates will remove dissolved oxygen from waterways in amounts that may be harmful to aquatic organisms.

Spills or runoff from field application for dust suppression into surface or groundwaters could create these low dissolved oxygen conditions that are detrimental to aquatic life. However given the proportion of lignin used in binding of minerals is normally in the range of 2-3 % of binder solids by weight the effects on fields are expected to be insignificant.

Little additional information is available in the published literature on the degradation pathways for sodium carbonate lignin in water, and no information was found on environmental accumulation or bioaccumulation of sodium carbonate lignin. Given that lignin derived from sodium carbonate pulping is not significantly modified from its natural form in wood we can expect natural processes for rotting wood such as soil microorganisms, enzymatic reactions, and ultraviolet (UV) radiation and wood fungi to contribute to their breakdown.

(c) Environmental impacts from its use and/or manufacture;

Manufacture:

As discussed, sodium carbonate lignin is derived from the spent liquor of the paper pulping process. In comparison to sulphite pulping, sodium carbonate pulping is considered more benign because it does not create the products of sulfate liquor decomposition (EPA 2017 Chemical Wood Pulping and the Owens-Illinois patent description). Historically lignin liquors were treated as waste and discarded or burned as an energy source. There has been considerable interest in bio-technology and recycling the lignin liquor. Given that sodium carbonate lignin is recovered from waste products of the paper pulp industry after manufacture, the likelihood of environmental contamination from its manufacture is reduced. However, there is still the possibility that sodium carbonate lignin from paper pulping operations or transportation activities could be spilled or lost to soils, nearby waterways, or environmentally-sensitive areas. The same possibility of spills exists in manufacturing facilities that produce mineral pellets for soil amendment, where sodium carbonate lignin liquor may be stored in bulk. As discussed in the responses to evaluation questions 10(b), large spills of sodium carbonate lignin could decrease the available oxygen in bodies of water.

Use:

Sodium carbonate lignin used as dust suppressants for minerals applied to the soil could contaminate waterways via runoff following a heavy rain event. As discussed, the primary concern regarding sodium carbonate lignin in waterways is their high BOD upon decomposition. If the sodium carbonate lignin is used as petitioned and sound soil application and incorporation practices are followed, then the standard formulation of 2-3% of binder solids in the mineral would not contribute significant lignin to cause concern. Alternative uses for lignin liquors are being investigated due to its non-toxicity and binding qualities in bio-products such as fully compostable thermoplastics and other packaging.

Misuse:

Misuse of sodium carbonate lignin could occur if more than 2-3% of binder was used in the mix formulation or very heavy application of the pelletized soil amendment were applied on soils or near natural water ways. However there is essentially a cost disincentive for adding more lignin to minerals or over-application of minerals for soil amendment due to extra cost of both the lignin and the mineral. Other forms of misuse would be negligent handling of the sodium carbonate liquor causing spills and improper disposal.

Disposal:

Sodium carbonate lignin liquor should be disposed using customary procedures for industrial waste as indicated on the MSDS. Sodium Carbonate lignin should not be discharged into municipal water treatment plants, streams, ponds, estuaries, oceans and other waters. This handling and disposal information is clearly identified on the MSDS which must accompany any sodium carbonate lignin product.

(d) Effects on human health; and

No references were found specific to sodium carbonate lignin. Lignin sulfonate, another lignin derivative is referenced here.

The U.S. EPA issued an exemption from the requirement of a tolerance for lignin sulfonates when they are used as inert ingredients pre- and post-harvest in agricultural production. This exemption is based on the conclusion that there is a '…reasonable certainty that no harm will result…" to the general public, infants, and children from aggregate exposures (includes all dietary, drinking water, and non-occupational exposures) to lignosulfonates.
Given sodium carbonate lignin contains primarily lignin very close to its natural state and sodium carbonate it is considered even more benign.

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

Livestock:
As stated in question # 8, under 21 CFR 573.600(a) and (b), the FDA Food Additives Permitted in Feed and Drinking Water of Animals, named types of lignin sulfonate may be used in a liquid form or a dry form in animal feeds.
As a soil amendment, given the small percentage (2-3%) used to pelletize minerals, and with no direct exposure, as it is applied directly onto soils, the impact on livestock of sodium carbonate lignin is expected to be minimal.

Soil:
Lignin derivatives break down by natural physical or microbiological processes, but may persist in the soil up to one year. Lignins are unlikely to accumulate in soil unless they are applied very frequently. Breakdown of lignin occurs in part because lignin is used as a carbon source by a variety of wood-decaying microorganisms. It is therefore likely that large amounts of lignin applied to soils could stimulate soil microbial activity. (adopted from NOSB 2011 Technical Evaluation Report Lignin Sulfonates)

The sodium and sodium carbonate content in the sodium carbonate lignin would be very soluble in water and could increase salinity and pH in soils potentially causing adverse effects to plants and soil organisms. The pH of the liquor ranges from 6 (slightly acidic) to 9 (mildly alkaline) and salinity is in the 5- 8% range. Example lab analyses for sodium carbonate lignin liquor are given in Appendix E.

Used in formulation with minerals as intended at 2 % binder solids (% wt. binder solids /% wt. processed mineral), this effect is not expected to be of concern. This formulation ratio represents 20 kg of binder solids in one tonne of final product of soil amendment, not significant to impact pH.

Simple mass balance calculations for salinity assuming the worst case (8 % by weight and all the sodium is present as pure sodium and not as sodium carbonate, which is not expected), show that estimated salinity levels in the final soil amendment product would be in the 1-2 kg/Tonne range. Salinity levels would be much lower than this if the binder solids are separated from the liquor solution to form a powdered product before use. This compares favorably with other soil amendments such as animal manures which can deliver as much as 6.5 kg/tonne (poultry). (2018 Chastain, Camberato, Skewes).

Precedence for acceptability of other lignin salts was identified in the response to question 8. Sodium lignosulfonate, magnesium lignosulfonate, ammonium lignosulfonate (with restrictions), and calcium lignosulfonate are allowed as crop production aides (2018 OMRI Generic Materials List) and as binders in animal feed (21 CFR 573.600(a) and (b), the FDA Food Additives Permitted in Feed and Drinking Water of Animals).

Organisms and aquatic life:

When lignin derivatives are discharged to waterways, their decomposition removes dissolved oxygen from water. The lack of dissolved oxygen is harmful to aquatic organisms and, depending on the amount of lignin that is discharged, can have a negative impact on aquatic organisms to varying degrees. (NOSB 2013 Technical Evaluation Report- Lignin Sulfonates)

11. Safety Information:

Provide 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 this information does not exist or is not applicable, the petitioner should state so in the petition.

An MSDS for sodium carbonate lignin is provided in Appendix D

A search for sodium carbonate lignin on the National Institute of Environmental Studies did not deliver any results. In terms of other lignin compounds, ammonium and sodium lignosulfonate substance reports were available.

12. Research Information:

Very limited research information was found for lignin derived from the soda ash or sodium carbonate pulping process either in support or contrasting our position as they represent only a small fraction of total pulp manufacturing worldwide. Given the assertion that they are equivalent substances, information found in the NOSB 2011 and 2013 Technical Evaluation Reports for lignin sulfonate was used frequently as noted throughout this petition.

A technical review was conducted by Khalil Jradi PhD. Chemistry, a subject expert, to confirm and summarize the information presented here. His report lists many references and is presented as Appendix C . The report takes the form of answering questions specific to this petition and his research and responses confirm the assertions made in this petition.

Presented here is research information found for sodium carbonate lignin and on other lignin derivatives pertinent to this petition, for their use as a binder for dust suppression.

- Research on the binding qualities and effectiveness of lignins and other alternatives.

IBA 1993 Kurt B. Albert Don Langford, PELLETIZING LIMESTONE FINES
A Study of the Benefits of Pelletized Limestone Fines in the Commercial and Agricultural Market

IBA 1991 Of Beer, Leather, and Beets – A Study of Alternative Binders in Agitation Pelletizing

IBA 2001 Jim Veverka, Robert Hinkle -A Comparison Of Liquid Binders For Limestone Pelletizing.

- Research on characteristics of lignin in residual liquors from pulping processes, confirming that lignin liquors are a heterogeneous mixture of lignin in natural form and in various states of delignification with hemicellulose and cellulose:

Chakar, Ragauskas , 2004, Review of current and future softwood Kraft lignin process chemistry. Institute of Paper Science and Technology, School of Chemistry and Biochemistry, Georgia Institute of Technology. Excerpt:
Numerous studies have been conducted to elucidate the nature of the residual lignin in pulps and dis-solved lignin. Some of the major conclusions that stem from these studies are that the nature of the residual lignin falls between that of the lignin in wood and dis-solved lignins, and those changes in lignin functional groups are to a large extent a function of the degree of delignification.

- Research on the Soda Ash /Sodium Carbonate pulping process with identification of differences and environmental benefits compared with sulfite pulping processes: This research confirms that the soda process is considered to be even more benign than Kraft and other sulfite pulping processes.

United States Patent 3954553 Owens-Illinois, Inc. (Toledo, OH), Non-sulfur pulping process for corrugating medium using sodium carbonate and sodium hydroxide.

Yayin, Irmak,1992 "Optimization of Sodium Carbonate-Sodium Hydroxide Pulping of Wheat Straw for Corrugating Medium Production" Western Michigan University, Master's Theses. 954.

EPA 2017 AP-42, CH 10.2: Chemical Wood Pulping

13. Petition Justification Statement:

Provide a “Petition Justification Statement,” which provides justification for any of the following actions requested in the petition:
A. Inclusion of a Synthetic on the National List (7 C.F.R. §§ 205.601, 205.603, 205.605(b))

We are requesting a revision to CFR§205.601(j)(4) on the basis that sodium carbonate lignin is an equivalent substance to lignin sulfonates. This assertion is made based on two grounds:

First, that lignin liquors derived from pulping are very broadly named and in fact represent a heterogeneous mixture of several organic and inorganic components and second that the beneficial active ingredient for dust suppression is lignin complexed with hemicellulose in pulping liquor and this complex is present in many different forms in lignin sulfonate liquors. It can be shown that the components of sodium carbonate lignin are already found in other liquors approved under the term ‘lignin sulfonate’ by the NOSB.

We present the basis for equivalency here:

Because lignin is bound to cellulose in plants, some form of extraction technology is necessary to access it. The resulting liquors from pulping are not a ‘clean’ homogeneous substance but instead are a heterogeneous mixture of lignin fragments, carbohydrates from the breakdown of hemicellulose and the residual inorganic chemicals used for cooking. Lignin is at different levels of delignification and complexing with hemicellulose and cellulose in this mixture. Adding to the situation is that lignins are very complex natural polymers and their exact chemical structure is not well understood. Because of its nature, this mixture is often referred to as a ‘soup’.

As a direct result, historically, naming of the lignin sulfonates derived from the various pulping processes has been based on the cooking chemicals used for delignification or the pulping process. These names were very broad based, rather than specific, and while attempts have been made to standardize the nomenclature there is confusion in identification and CAS numbering (at least 12 CAS numbers can be found for lignin and lignosulfonate derivatives often naming the two under the same number).

For example, the sulfite process produces wood pulp by using various salts of sulfurous acid to extract the lignin from wood chips. The salts used in the pulping process are either sulfites (SO32−), or bisulfites (HSO3−), depending on the pH. The counter ion can be sodium (Na+), calcium (Ca2+), potassium (K+), magnesium (Mg2+) or ammonium (NH4+). The spent sulfite liquor (from which the lignosulfonate is recovered for re-use) contains lignin as lignosulfonate, sugars and inorganic salts. It follows then, that sodium lignosulfate was named based on the sulfite process that uses sodium as the counter ion and so on for calcium lignosulfonate, magnesium lignosulfate, etc.
Sodium carbonate lignin (also known as soda lignin) was likewise named and defined by the cooking liquids used in the soda pulping process; sodium carbonate.

This example serves to identify that when lignin sulfonates were named and reviewed in the past they were not rigidly describing a specific chemical, the exact pulping process or the mixture of lignin compounds present. In fact, we have the opposite; they are arbitrarily naming a complex mixture.
We believe that the intent in approving lignosulfonate for crop production was to capture the benefits of the natural lignin complexes as the active binding ingredient for use as a dust suppressant. It is the lignin complexed with the hemicellulose that is the active binding ingredient for dust suppression (Ref K. Jradi PhD. Appendix C), the residual salts and sulfonating of lignin are immaterial. Note that in lignin sulfonate liquors the hemicellulose is not even named even though it is integral to its binding qualities.
Furthermore, it can be shown that simple lignin fragments and sodium carbonate and sodium hydroxide produced in the soda process are in fact also present in the lignin sulfonate liquors of other lignin liquors, namely Kraft lignin and sodium lignosulfonate, already accepted by the NOSB. The lignin compounds are also closer to their natural form in sodium carbonate lignin.

Historically there is recognition of the naming issue and a strong precedence for expanding the definition of allowable lignin compounds for organic crop production. The number of allowable lignin sulfonates, as listed in the current OMRI directory, has expanded over time to include several salts, including sodium lignosulfonate, magnesium lignosulfonate, ammonium lignosulfonate, and calcium lignosulfonate (OMRI, 2019) even though these lignosulfonate salts are not specifically identified on the National List. (2013 TR NOSB line 143). This recognizes that lignin sulfonates are prevalent as a salt of lignin sulphonate not as simply lignin sulphonate.

Therefore, we contend that adding un-sulphonated lignins in the annotation of 7 CFR§205.601(j)(4) is simply expanding the existing definition of lignin compounds to include another form of benign lignin already present in the loosely defined liquors of lignin from pulping. We believe because of the lower production volumes relative to other pulping processes, it was simply not considered in the original reviews by the NOSB.

- In review, as well as being equivalent, sodium carbonate lignin meets all of the 7 criteria for approval under section 3.5:

(1) The potential of the substance for detrimental chemical interactions with other materials used in organic farming systems;

We have established that no chemical interactions occur with the minerals that are pelletized as the primary mode of action is in binding smaller dust compounds by adsorbing them to the lignin compound and forming larger heavier complexes that are not so friable.

(2) The toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment;
3) The probability of environmental contamination during manufacture, use, misuse or disposal of the substance;
(4) The effect of the substance on human health;
(5) The effects of the substance on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops, and livestock;

Section 10 (a) to (e) of this petition established no concerns with respect to sodium carbonate lignin and items (2) to (5) above for the intended use as a dust suppressant and further established that sodium carbonate lignin is a produced from a benign form of wood pulping.

(6) The alternatives to using the substance in terms of practices or other available materials;

Alternatives as binders in pelletization for dust suppression include:

Lignin sulfonates – Allowable synthetic under NOP 205.601(j) (4) as dust suppressant and chelation agent. Lignosulfonate is another form of lignin derived from trees that comes as a by-product of the paper making industry. It is generated by a chemical pulping process using a sodium sulfite solution. They are used for their binding, dispersing, and emulsifying properties. Lignosulfonate is currently allowed and used in organic production as a binder for pelletization of minerals to suppress dust during application. It is considered a superior binder (IBA 2001 Jim Veverka, Robert Hinkle) to other allowable organic options in that the pellets better withstand attrition loss, crushing and agitation breakdown during handling and transportation.
Any breakdown of pellets incurred during handling of soil amendment minerals directly co-relates to potential dust created during field broadcasting and other farming activities such as load transferal. Therefore the quality of the binder is important to reducing nuisance dust, meeting air quality guidelines for fine particulate matter and economic losses for the farmer due to driftage or uneven application.

Sodium Carbonate lignin has been used interchangeably with lignin sulfonate and is considered an equivalent substance for binding.
Another consideration in favor of lignin liquors is that using them for dust supression is a very beneficial reuse of a surplus product.

Brewex – An organic modified starch brewery by-product containing glucose, maltose, and maltodextrin. It is an evaporative product derived from beer production residuals containing the above carbohydrates, protein, and water. As a product of fermentation, Brewex has the potential to meet organic standards as an allowable input for organic production if made from solely organic sources, but it is currently not specifically listed on the OMRI generic materials list and does not have significant usage.

Molasses – Molasses is eligible as plant extracts which are listed in the NOP rule (205.105). It is a non-synthetic generic material allowed with restrictions. It may be from non-organic sources but may not contain any prohibited substances. Molasses is a by-product of cane or beet sugar refining. It is residual heavy syrup left after the crystallization process. Although molasses has acceptable performance as a binder for pellitization (IBA 1991), its desirability and demand as a food product makes molasses very expensive and not readily available. It does not withstand crushing and breakdown over time and also has the negative characteristic of attracting vectors due to the sugar content.

(7) Its compatibility with a system of sustainable agriculture

The importance of lignin compounds in dust suppression for crop production:

When applying common ground or pulverized agricultural minerals such as lime and gypsum for organic crop production, several problems are prevalent. These minerals are difficult to apply with conventional rotary broadcasting spreaders or trough-type spreading devices. With these mechanical spreaders, the limestone tends to bridge and rat-hole in the spreader causing plugging and this and the fact that fine grounds are difficult to broadcast, causes very uneven distribution.

In spreading the mineral on the field, there is also the difficulty of windage loss and the creation of clouds of airborne dust. As well as losses, fine dust or particulate matter (small particles under 10 micrometers in diameter) released during spreading may affect compliance with the Clean Air Act, since the EPA includes these compounds as one of the six ‘criteria pollutants’ used to monitor and regulate air quality throughout the United States. Control of fine particulates through pelletization would thereby be in direct support of state and federal air emissions standards (2012 National Ambient Air Quality Standards (NAAQS) for Particulate Matter (PM)) and protect the producer from potential losses and nuisance to neighbors.

Additionally, with the coarse grit of ground minerals, the availability to the soil is slow, sometimes taking several months to totally break down. In comparison, research has shown that the pellets which are comprised of more finely pulverized minerals (100 mesh size or finer) break down more effectively when exposed to rainfall or moisture, and are more immediately available to support plant life. (IBA 1993 Albert, Langford)

Lignin derivatives are a more readily available and beneficial binder than the other alternatives. The NOSB committee demonstrated support for relisting lignin sulfonate until 2022 as it met all the category evaluation criteria for relisting. Sodium carbonate lignin is well within the same acceptability criteria in 7 CFR 205.601(j)(4) afforded to lignin sulfonates for dust suppression and fully meets the required criteria on its own merits.

- **Provide evidence that the current annotation is flawed, unnecessary, or outdated.**

In requesting a change to have sodium carbonate lignin specifically named in 7 CFR 205.601(j)(4) we are simply requesting clarification of the forms of lignin allowed. Restricting the annotation to “lignin sulfonate” does not acknowledge the fact that the naming conventions for lignin liquors are very broad in that they are simple names for a complex mixture of lignin compounds. This misrepresents the true nature of lignin compounds. As we have shown, the definition of allowable lignin compounds has already been expanded in the past by materials review agencies to include the salts of lignin sulfonates such as sodium lignin sulfonate for the simple fact that lignin sulfonates are usually present with a salt. It would also be beneficial to have these lignin sulfonate salts named in the annotations as suggested in section A1.

We are requesting that sodium carbonate lignin be evaluated on the basis that it is another form of benign lignin and the components are already in the mixtures approved by the NOSB. It recognizes that other forms of lignin sulfonates have been added in the past and it already exists in these mixtures. This is less about introducing a new material and more about identifying it on the national list for clarity so that it may be considered by organic certifying bodies and materials review agencies such as OMRI as acceptable for organic crop production.

In conclusion, sodium carbonate lignin is very beneficial for organic crop production and is a benign form of lignin derived from a simple pulping process that does not use sulfur. It is well within the same acceptability criteria afforded by the NOSB to lignin sulfonates in 7 CFR 205.601(j)(4). We believe it has not been considered previously simply because it is not as ubiquitous as lignin sulfonates, which compromise the vast majority of lignin's derived from pulping.

References:

IBA 1993 Albert, Langford, PELLETIZING LIMESTONE FINES
A Study of the Benefits of Pelletized Limestone Fines in the Commercial and Agricultural Market

IBA 1991 Of Beer, Leather, and Beets – A Study of Alternative Binders in Agitation Pelletizing

IBA 2001 Jim Veverka, Robert Hinkle -A Comparison Of Liquid Binders For Limestone Pelletizing-

United States Patent 3954553 Owens-Illinois, Inc. (Toledo, OH), Non-sulfur pulping process for corrugating medium using sodium carbonate and sodium hydroxide

EPA 2017 AP-42, CH 10.2: Chemical Wood Pulping

CGSB amended 2018. Can/CGSB-32.311-2015: Organic Production Systems Permitted Substances Lists. Canadian General Standards Board. https://www.certifiedorganic.bc.ca/standards/docs/CAN-CGSB-32.311-2015E.pdf

CPWA. 2005. Dust Control for Unpaved Roads, A Best Practice by the National Guide to Sustainable Municipal Infrastructure. Canadian Public Works Association. Retrieved on December 14, 2010 from http://gmf.fcm.ca/files/Infraguide/Roads_and_Sidewalks/dust_control_unpaved_rd.pdf.

NOSB 2011 Technical Evaluation Report Lignin Sulfonates www.ams.usda.gov

NOSB 2013 Technical Evaluation Report Lignin sulfonates www.ams.usda.gov

OMRI 2018. OMRI Brand Name Products List and Generic Materials List, Organic Materials Review Institute. Eugene, Oregon. Retrieved on Dec 15, 2018 from https://www.omri.org/ubersearch/results/lignin%20sulfonates?type[]=opd_generic_listing

Yayin, Irmak,1992 "Optimization of Sodium Carbonate-Sodium Hydroxide Pulping of Wheat Straw for Corrugating Medium Production" Western Michigan University, Master's Theses. Soda ash pulping chemistry Pgs. 18,19 and 35.

Chakar, Ragauskas , 2004, Review of current and future softwood Kraft lignin process chemistry. Institute of Paper Science and Technology, School of Chemistry and Biochemistry, Georgia Institute of Technology. Section 5.0 Nature of residual and dissolved lignin in kraft pulps.

2018 Chastain Camberato, Skewes Chapter 3b Poultry Manure Production and Nutrient Content,

Table 3-1 pg 3-b-2 https://www.clemson.edu/extension/camm/manuals/poultry/pch3b_00.pdf

2019 Khalil Jradi Assistance for the Sodium Carbonate Lignin petition submitted by Legnochem- Appendix C

Appendices:

Appendix A: NOSB Technical Evaluation Panel Report Lignin Sulfonate 2011
Appendix B: NOSB 2013 Technical Evaluation Report Lignin sulfonates
Appendix C: Technical Review of Sodium Carbonate Lignin by Khalil Jradi, PhD. Chemistry April 2019
Appendix D: MSDS's sodium carbonate lignin and Labels
Appendix E: Example lab analyses of sodium carbonate lignin liquor

APPENDIX A:

NOSB Technical Evaluation Panel Report- Lignin Sulfonate 2011

Lignin Sulfonate

Crops

Identification of Petitioned Substance

Chemical Names:
Lignin sulfonate

Other Names:
lignosulfonate
lignosulfuric acid
lignosulfonic acid
LST 7
Ligninsulonic acid
Poly(lignosulfonic acid)
Protectol W
Sulfite lignin
(NLM, 2011a)

There are also various salts of lignin sulfonate listed in the CAS Numbers section.

Trade Names:
Lignosite® – Georgia-Pacific (Georgia-Pacific West, Inc., 2000)
BorrePlex – LignoTech USA, Inc. (OMRI, 2010)
Phyto-Plus® Plant Stimulator – Baicor L.C. (OMRI, 2010)
SHADOW – LignoTech USA, Inc. (OMRI, 2010)
Orzan – ITT Rayonnier (Sugar and Spotts, 1986)

CAS Numbers:
8062-15-5

Lignosulfonate salts:
8061-51-6 (sodium lignosulfonate)
8061-54-9 (magnesium lignosulfonate)
8061-53-8 (ammonium lignosulfonate)
8061-52-7 (calcium lignosulfonate)
(U.S. EPA, 2010a)

Other Codes:
705707 (USEPA PC Code [U.S. EPA 2010b])
160226 (EPA Reference ID)
705705, 705708–705714 (U.S. EPA PC Code [U.S. EPA, 2010b], various lignosulfonate salts)
1522 (CODEX Alimentarius Commission INS Number, calcium lignosulfonate)

Characterization of Petitioned Substance

__Composition of the Substance__:

Lignin is a constituent of woody plants that functions as a strengthening element. Lignin sulfonate is a derivative of lignin, where the lignin has been sulfonated in a wood pulping process (Zhor and Bremner, 1999). Lignin sulfonate has the chemical formula $C_{20}H_{26}O_{10}S_2$ (NLM, 2011b) and its structure is presented in Figure 1. However, lignin sulfonate may be composed of a variety of sulfonated aromatic alcohols which make up lignin polymers, including *p*-coumaryl alcohol, sinapyl alcohol, and coniferyl alcohol (FAO, 2008). The lignin molecule is complex and not well understood in spite of its prevalence (Pure Lignin, 2010). The sulfonate complex may be in association with calcium, magnesium, ammonium, or sodium (U.S. EPA, 2010b).

The National List of Allowed and Prohibited Substances (hereafter referred to as the National List) identifies lignin sulfonate as a synthetic substance allowed for use in organic production (7 CFR 205.601). Because the lignin sulfonate molecule is negatively charged, it typically complexes with various cations to form lignin sulfonate salts. Four specific lignin sulfonate salts are included in the Generic Materials List published by the Organic Materials Review Institute (OMRI): sodium lignosulfonate, magnesium lignosulfonate, ammonium lignosulfonate, and calcium lignosulfonate (OMRI, 2010). Although these salts are not specifically named in the National List, this Technical Report provides relevant information about them when available.

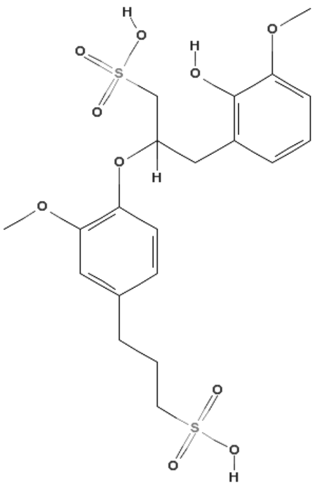

Figure 1. Chemical Structure of Lignin Sulfonate (NLM, 2011b)

Properties of the Substance:

A molecular weight of 490.5 g/mol has been reported for lignin sulfonate (NLM, 2011b). Other reports on the lignin sulfonates as a group state that they may have molecular weights ranging from 1,000 to 20,000 daltons, or higher (up to 100,000 daltons in some cases) depending on their composition (Zhor and Bremner, 1999; Hawley, 1981). Weight-average molecular weights of calcium lignosulfonate are reported to range from 40,000 to 65,000 (unitless). Calcium lignosulfonate is soluble in water and insoluble in organic solvents (FAO, 2008).

Other physical and chemical properties of lignin sulfonate are presented in Table 1. The properties presented in Table 1 describe lignin sulfonate generally, unless a specific salt is otherwise indicated.

Specific Uses of the Substance:

Lignin sulfonate may be used in organic crop production as a plant or soil amendment (dust suppressant, chelating agent) and a floatation agent for postharvest handling of products (e.g., pears). Chelating agents are large, organic molecules that are used to envelop highly-reactive trace metal ions. The purpose of chelates is to incorporate metal ions into a soluble but bound form that is capable of supplying nutrients to plants. As the chelate breaks down, the metal ion micronutrients are slowly released into the soil in a bioavailable form that may be taken up by the plant (Jones and Jacobsen, 2009). Two manufacturers produce products containing lignin sulfonate—LignoTech USA, Inc. and Baicor, L.C. (OMRI, 2010). LignoTech manufactures five products and Baicor, L.C. manufactures one product (OMRI, 2010).

Lignin sulfonates have also been investigated for their potential as chelating agents for the complexation of metal ions, including copper, magnesium, and mercury, for the purpose of environmental remediation. Garcia-Valls et al. (2001) cited the biodegradability and relatively inexpensive nature of the lignin sulfonates as factors supporting their use in remediation. Lignin sulfonates have also been used in bioremediation at dairy operation facilities and meat and seafood canneries. Lignin sulfonates were applied to waste streams at the facilities to help remove dairy and seafood waste. The lignin sulfonates formed complexes with the waste materials, which then precipitated out of wash solutions. This process allowed for diversion of some food waste from waterways. The resulting food waste/lignin sulfonate complex was then used in animal feed (USDA, 1969).

Table 1. Chemical Properties of Lignin Sulfonate

Chemical or Physical Property	Value
Color	Light tan to dark brown* ‡ † (CAMEO, Undated-a; CAMEO, Undated-b)
Physical State	Solid (powder) (Hawley, 1981)
Odor	Odorless (CAMEO, Undated-a)
Melting Point	Decomposes at >200°C (>392°F) (Hawley, 1981)
Boiling Point	Exists in a solid state
Solubility	Soluble in water† (FAO, 2008)
Stability	Soil half-life up to one year depending on chemical species and soil flora* † (Selin et al., 1975)
Reactivity	Lignin sulfonates are corrosive to aluminum and aluminum alloys in the absence of calcium carbonate (CPWA, 2005)
Oxidizing or Reduction Action	React as acids to neutralize bases. Usually do not react as reducing or oxidizing agents (CAMEO, Undated-a)‡
Flammability/Flame Extension	Flash point data not available although probably combustible (CAMEO, Undated-a) ‡
Explodability	Dust explosions may occur if fine particles are mixed with air in the presence of an ignition source. Ignition temperature is approximately 250–300°C (482-572°F) * (Georgia-Pacific West, Inc., 2000)

*Sodium lignosulfonate
‡Ammonium lignosulfonate
†Calcium lignosulfonate

Calcium lignosulfonate may be used as an inert ingredient or adjuvant (mixing agent/sticking aid) in pesticide products, except for those exempt under Section 25(b) of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)[1] (OMRI 2010; CFR, 2003a; CFR, 2003b; CFR, 2003c). Calcium lignosulfonate is also used as an encapsulating agent or carrier for fat-soluble carotenoids, vitamins, and other functional ingredients in foods such as vitamin drinks, fruit-based beverages, hard candies, and dairy products (Toledo and Kuznesof, 2008). As discussed in the "Composition of the Substance" section, other lignin sulfonate salts are included in the OMRI Generic Materials List (OMRI 2010), but little specific information is available about them.

Approved Legal Uses of the Substance:

Lignin sulfonate is currently included on the National List as a synthetic substance allowed for use in organic production (7 CFR 205.601). Lignin sulfonate may be used in organic crop production as a plant or soil amendment (dust suppressant, chelating agent, or floatation agent) or a flotation agent in postharvest handling (see 7 CFR 205.601(j)(4) and 7 CFR 205.601(l)(1)). The OMRI generic materials list includes the following lignin sulfonate salts: sodium lignosulfonate, magnesium lignosulfonate, ammonium lignosulfonate, and calcium lignosulfonate (OMRI, 2010). These lignosulfonate salts are not specifically identified on the National List.

Calcium lignosulfonate (CAS No. 8061-52-7) and sodium lignosulfonate (CAS No. 8061-51-6) may be used as inert ingredients in pesticide products. These inert ingredients are on EPA's inert ingredients list (List 4B) which, in combination with List 4A, was used as a reference for allowed inert ingredients in organic pesticide products. In 2006, EPA changed its classification system for inert ingredients, but lists 4A and 4B are still maintained for their use by the NOP. The NOP still allows inert ingredients on these lists to be used as inert ingredients in pesticide products unless the ingredients were removed following EPA

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[1] FIFRA is the federal law that regulates pesticide products in the United States and is administered by the U.S. EPA.

reassessment. Calcium lignosulfonate and sodium lignosulfonate have not been removed from the EPA List 4B and are therefore allowed for use as inert ingredients in pesticide products (NOSB, 2009).

Ammonium lignosulfonate is allowed, with restrictions, for use as a nutrient chelate in organic fertilizer products. Formulated fertilizer products that contain ammonium lignosulfonate may not make nitrogen claims on the label and/or the contribution of ammonium lignosulfonate to the total nitrogen content of the formulated product must be less than 1percent (OMRI 2010; CFR, 2003a; CFR, 2003b; CFR, 2003c). Lignin sulfonate is exempt from the requirement of a tolerance when used as an inert ingredient in pre- and post-harvest agricultural production and as an inert ingredient applied to animals (CFR, 2004a; CFR, 2004b). Tolerances are acceptable levels of pesticide residues on food products that are set by the U.S. EPA, and enforced by the USDA and FDA. According to 40 CFR 180.900, "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."

Action of the Substance:

Lignin sulfonate acts as a dust suppressant by its large size and affinity for binding with other polar and nonpolar compounds. The smaller dust compounds adsorb to the lignin sulfonate and form a larger, heavier complex that is not as friable, which suppresses the dust (CWPA, 2005). Lignin sulfonate is used as a micronutrient chelate because it is a large compound with multiple polar and nonpolar moieties. The relatively smaller, charged micronutrient ions, such as boron, manganese, and iron, are bound to the large lignin sulfonate molecule and are slowly released into the soil in a bioavailable form (Jones and Jacobsen, 2009). Lignin sulfonate will help stabilize emulsions by acting as a surfactant. Lignin sulfonate dissolved in water is mixed with oil and preferentially adsorbs to the oil molecules, forming a barrier at the interface between the oil and water, which stabilizes the emulsion (Gundersen and Sjoblom, 1999; LignoTech, 2009). When used as a flotation aid, lignin sulfonate is added to the dump water to increase the density of the water. This is necessary for fruits like pears that may be heavier than water. Increasing the density of the water with lignin sulfonate allows the pears to float, and therefore the pears are less likely to be damaged in processing (Agar and Mitcham, 2000).

Combinations of the Substance:

Through its use as an emulsifier and adjuvant, lignin sulfonates (calcium lignosulfonate and sodium lignosulfonate) may be combined with various pesticide active ingredients that act as insecticides or herbicides (NOSB, 2009; OMRI, 2010; CFR, 2003a; CFR, 2003b; CFR, 2003c).

Status

Historic Uses:

Lignin sulfonate has been used in organic agricultural production as a dust suppressant, chelating agent for micro- and macronutrient fertilizer applications, flotation agent in pear production, and as an emulsifier and stabilizer for pesticide applications. A previous technical report for lignin sulfonate was created as part of the 1995 petition process to add lignin sulfonate to the National Organic Standards Board (NOSB) National List (NOSB, 1995).

Lignin sulfonate has been investigated for its potential as a chelating agent in the environmental remediation of heavy metals and in the remediation of food processing wastes (Garcia-Valls et al., 2001; USDA, 1969). Lignin sulfonate also has been used as an encapsulating agent for vitamins and other ingredients in food products (Toledo and Kuznesof, 2008).

Lignosulfonates have a variety of industrial applications. One of the main applications of lignosulfonates is in the concrete industry, where they may be used as dispersing agents and to delay the setting of concrete. In other industries, they may be used as additives in oil well drilling, dispersants for dyestuffs, cleaning agents, and as a partial substitute for phenol in the manufacture of adhesives. Sodium lignosulfonate is potentially useful in inhibiting corrosion and scale formation in recirculating cooling water systems (Ouyang et al., 2006).

OFPA, USDA Final Rule:

Lignin sulfonate is included within the scope of the Organic Foods Production Act of 1990 by implied inclusion in the group, "…an active synthetic ingredient in the following categories: copper and sulfur compounds…"

Lignin sulfonate is explicitly identified in the National List in 7 CFR Section 205, as follows:

- 205.601(j)(4) – Lignin sulfonate - chelating agent, dust suppressant, floatation agent

- 205.601(l) – As floating agents in postharvest handling; (1) Lignin sulfonate

International:

Some international organizations allow the use of lignin sulfonate in organic food production. The Canadian General Standards Board allows the use of lignin sulfonate as a dust suppressant, formulant ingredient, and chelating agent (Canadian General Standards Board, 2009).

The International Federation of Organic Agriculture Movements (IFOAM) includes calcium lignosulfonate on its "Indicative List of Substances for Organic Production and Processing." No other lignin sulfonates are included (IFOAM, 2008). As of 2009, calcium lignosulfonate is allowed by the CODEX Alimentarius Commission as a food additive, and the compound has been assigned INS Number 1522 (Codex Alimentarius Commission, 2010).

Until 2008, lignin sulfonate was not allowed to be used in the production of certified organic products exported to Japan from the United States. In 2008, the Ministry of Agriculture, Forestry, and Fisheries (MAFF) in Japan lifted the ban of lignin sulfonate on crops imported to Japan. However, the products containing lignin sulfonate must be accompanied by an export certificate and must be imported by a JAS-certified importer (USDA, 2009). Lignin sulfonate is not specifically discussed by the European Economic Community Council Regulations.

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

Evaluation Question #1: What category in OFPA does this substance fall 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). Lignin sulfonate is listed by inference as part of the group, "copper and sulfur compounds" in the OFPA, Section 2118 (c)(1)(B)(i).

(B). Lignin sulfonate is a synthetic inert ingredient that is not classified by EPA as an inert of toxicological concern. Lignin sulfonate (and the lignosulfonate salts) are exempt from the requirement of a tolerance under 40 CFR parts 180.910 and 180.930.

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)).

Lignin sulfonates are produced from the process of sulfite chemical pulping. Sulfite pulping involves cooking softwood chips under pressure in sulfur dioxide-containing cooking liquors. When the cooking process is complete, sulfonated lignin is collected as a liquid by-product in the spent liquor, while the pulp is used for paper production. The lignin sulfonates that result from the spent liquor of the sulfite pulping process must be further purified to remove excess sugars. This is done by fermentation of the liquor, followed by heating to remove the alcohol generated. The resulting lignin sulfonate polymers can have high molecular weights ranging from less than 1,000 to more than 100,000 daltons (Zhor and Bremner, 1999; Westvaco Corp., 1987).

Lignin sulfonates may also be obtained from the Kraft pulping process; these are referred to as Kraft lignins. Kraft pulping is similar to sulfite pulping, but involves treating the wood at high temperature and pressure in a water solution containing sodium sulfide and sodium hydroxide. This process dissolves lignin into a soluble salt which dissolves in the pulping liquor. The lignin is removed by precipitation from the liquor using carbon dioxide (CO_2). The Kraft lignins must then be sulfonated after extraction by reacting the material with bisulfate or a sulfite compound (Gundersen and Sjoblom, 1999; U.S. EPA, 1990).

A third pulping process, acid sulfite pulping, is similar to Kraft pulping, but different chemicals are used. Sulfurous acid, used in place of sodium hydroxide, is combined with sodium, magnesium, calcium, or ammonium bisulfite. After the cooking is complete, the pulp is separated from the spent liquor, which may then be treated to obtain various chemical materials (U.S. EPA, 1990).

Evaluation Question #3: Is the substance synthetic? 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).

Lignin exists naturally in all woody plants as a structural and strengthening component. Because lignin is integrated into the plant cell wall, there are no natural processes that liberate lignin other than natural decomposition of wood by microorganisms. Lignin sulfonates are produced from the application of pressure and heat to wood in the presence of sulfur dioxide or by the addition of alkali and various acids and sulfates, as described under Evaluation Question #2. These are not naturally-occurring processes. Therefore, lignin sulfonates are synthetic (U.S. EPA, 1990; Gundersen and Sjoblom, 1999).

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

Lignosulfonates discharged into water bodies may cause foaming and discoloration. Due to their high biological oxygen demand (BOD) during breakdown in water, lignosulfonates will remove dissolved oxygen from waterways in amounts that may be harmful to aquatic organisms (CPWA, 2005). Little additional information is available in the published literature on the degradation pathways for lignosulfonates in water.

The half-life of lignosulfonates in soil, as evidenced by the loss of sulfates or sulfonic acid groups, is up to one year. Soil microorganisms, enzymatic reactions, and ultraviolet (UV) radiation contribute to the breakdown of lignosulfonates. The structure of lignosulfonates may be altered by wood-rotting fungi, with polymerization being the main pathway, based on a decrease in phenolic hydroxyl groups (Selin et al., 1975). Laccase, an enzyme produced by fungi, increased degradation of lignosulfonates to low-molecular weight fractions under laboratory conditions (Cho et al., 2004). In addition to microbial decomposition, enzymatic oxidative reactions contribute to the early breakdown process of lignosulfonates. Light (UV radiation) also hastens the degradation of lignosulfonates by creating radicals capable of degrading the lignosulfonate molecular structure. This breakdown process yields lower molecular weight lignosulfonate fragments and CO_2. The CO_2 may account for 15–20%of the original organic carbon. As lignosulfonates degrade, they become more susceptible to further degradation by microbial populations. Due to the complex and heterogeneous structures of lignosulfonates, detailed information about breakdown products is difficult to describe (Lauten et al., 2010). Given that lignin is a naturally-occurring component of wood, once the sulfonic acid groups have been cleaved, the lignin that remains would likely be broken down in a manner very similar to that of rotting wood.

Evaluation Question #5: 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)).

Sodium lignosulfonate is relatively low in toxicity based on results of tests in laboratory animals, including rats, rabbits, and guinea pigs (Luscombe and Nicholls, 1973; Marcus and Watts, 1974). However, high doses of sodium lignosulfonate have been found to cause adverse health effects in laboratory animals. Rats that were given drinking water containing purified sodium lignosulfonate at a 10 g/100 ml concentration for 16 weeks had skin lesions at the bases of their tails, decreased weight gain, increased leukocyte counts, and increased kidney, spleen, and liver weights (Luscombe and Nicholls, 1973). In a study with guinea pigs and rabbits administered sodium lignosulfonate at a 1 percent concentration for a two- to six-week period, a high percentage of the animals developed ulcerative colon disease (Marcus and Watts, 1974). A median lethal oral dose of greater than 40 g/kg has been reported for rats (Luscombe and Nicholls, 1973). This dose corresponds to the U.S. EPA Toxicity Category IV for oral exposure (greater than 5000 mg/kg), which is the lowest toxicity category (U.S. EPA, 2007).

Results of a 28-day oral toxicity study in which calcium lignosulfonate was incorporated into the diet of rats at target doses of 0, 500, 1500, or 4000 mg/kg body weight per day showed no observed adverse effects other than chronic inflammation of the rectum at the highest dose level (4000 mg/kg-day). The no-observed-adverse-effect level (NOAEL) from this study was identified as 1300 and 1350 mg/kg-day for males and females, respectively (Munro and Baines, 2009).

In a 90-day study with Wistar rats dosed with calcium lignosulfonate in the diet at target doses of 0, 500, 1000, and 2000 mg/kg-day, the rats showed no adverse clinical signs or organ weight changes following complete pathological evaluations. Test results for primary immune response in the rats were normal. The only observed adverse effect was a dose-related increase in the incidence of histiocytosis (abnormal increase in the number of immune cells) of the mesenteric lymph nodes in male and female rats, with no observed histiocytosis in other lymph tissues. The Joint FAO/WHO Committee reviewed the finding of histiocytosis and concluded that it does not represent an adverse effect, based on findings with other compounds with similar properties (Munro and Baines, 2009).

No evidence of genotoxicity was found for calcium lignosulfonate in *Salmonella typhimurium* and *Escherichia coli* assays, and in a test for chromosomal aberration in Chinese hamster cells. No developmental effects were found in a study with calcium lignosulfonate and pregnant female Wistar rats. The no-observed-effect level (NOEL) for reproductive effects was identified as 1000 mg/kg-day (Munro and Baines, 2009).

Lignin sulfonates are soluble in water, so it is possible for dissolved lignosulfonates to enter waterways through direct contamination or soil runoff. Lignosulfonates in water may be toxic to fish. A 48-hour LC_{50} of 7,300 parts per million (ppm) was observed by Roald (1977) for rainbow trout. As lignosulfonates break down in water, they consume dissolved oxygen in the water due to their high BOD, which may adversely affect aquatic organisms through a decrease in available oxygen (CPWA, 2005; Jones and Mitchley, 2001). Due to the acidic pH of lignosulfonates, large spills to waterways may also affect pH of waterways.

In the previous technical report (NOSB, 1995), a letter from the petitioner addresses concerns with dioxin as a contaminant from the process of paper pulping. Dioxin is a highly-toxic contaminant that is considered a likely human carcinogen (U.S. EPA, 2010c). The petitioner noted that dioxins are generally associated with the Kraft pulping process, and that dioxins are produced as part of pulp bleaching. The petitioner (Western Chemicals) noted that the Georgia-Pacific Corp. generates its lignosulfonates using the bisulfite pulping process (NOSB, 1995). The petitioner also explained that the sulfite liquor, which contains the lignosulfonates, is removed from the pulp before the bleaching process; thus, it is not likely that dioxins would be found in the lignosulfonates generated from this process (NOSB, 1995). In addition, the petitioner reported that they had analyzed their lignosulfonate products for dioxins and furans, and have not detected the contaminants in their lignosulfonate products above the level of detection (NOSB, 1995).

Georgia-Pacific Lignosite® 100, 260, 431-H, and 458 have been classified as biodegradable, with a hazardous decomposition product of sulfur dioxide (SO_2), which can adversely affect the respiratory system (Ash and Ash, 2004; U.S. EPA, 2011b). Selin et al. (1975) commented on the recalcitrant (resistant to degradation) nature of lignosulfonates, but also showed that many wood-decomposing microbes could break down lignosulfonates. As described in the Action of the Substance section, lignin sulfonates bind strongly to smaller particles in the soil or water. Once adsorbed to the soil, lignosulfonates will be degraded by soil microorganisms. Lignosulfonates may persist for six months to one year when used for dust suppression before they break down (CPWA, 2005; Selin et al., 1975).

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

<u>Manufacture:</u> Spent sulfite liquors from the paper pulping process contain lignin sulfonate. Before the widespread use of lignin sulfonates, these liquors were treated as waste from the sulfate pulping process and discarded or burned for energy recovery. Given that lignin sulfonate is recovered from waste products of the paper pulp industry after manufacture, the likelihood of environmental contamination from its manufacture is reduced. However, there is still the possibility that spills of effluent from paper pulping operations could contribute large amounts of lignin sulfonate to soils, nearby waterways, or environmentally-sensitive areas.

<u>Use:</u> Lignin sulfonates used as dust suppressants or in chelates applied as plant nutrients to the soil may contaminate waterways via runoff following a rain event. The primary concern regarding lignin sulfonates in waterways is their high BOD upon decomposition. This causes removal of dissolved oxygen from the water and impacts aquatic organisms (CPWA, 2005).

<u>Misuse:</u> Dust explosions may occur if finely-divided lignin sulfonate is mixed with air in the presence of an ignition source. Excessive accumulation of dust should be avoided to help prevent explosions (Georgia-Pacific West, Inc., 2000). Decomposition of lignin sulfonate can release SO_2, which is an eye and airway irritant (Sullivan and Krieger, 1992; Georgia-Pacific West, Inc., 2000). Excessive amounts of lignin sulfonate applied to roads for dust suppression or large amounts applied just prior to rainfall events may increase the potential for lignin sulfonate to runoff to waterways.

<u>Disposal:</u> Lignin sulfonate-treated dump water for pear processing may need to be processed in a treatment system before its disposal. The goal for treatment of these waters is reduction in BOD to a level that does not impact aquatic life (McLellan and Padilla-Zakour, 2005). Untreated dump water could adversely affect aquatic organisms by competing for dissolved oxygen. In the case of spills or accidents involving lignin sulfonate, the area should be washed with water to dilute the spill (Georgia-Pacific West, Inc., 2000). To the extent possible, care should be taken to ensure that wastewater does not flow directly to water bodies. For spills, waste disposal methods include customary procedures for industrial waste treatment (Georgia-Pacific West, Inc., 2000). Spills or releases of lignin sulfonate are not subject to the

reporting requirements of the Federal Superfund Amendments and Reauthorization Act (SARA) of 1986 (Georgia-Pacific West, Inc., 2000).

Other: Lignin sulfonates have been investigated for their potential role as chelating agents for the complexation of metal ions, including copper, magnesium, and mercury, for the purpose of environmental remediation. The biodegradability and relatively inexpensive nature of the lignin sulfonates were cited as factors that support their use in remediation (Garcia-Valls et al., 2001). In a report on lignin and its uses by USDA, lignosulfonates were discussed as treatments for food waste from milk processing plants and meat or fish canneries. The lignosulfonate complexes form a precipitate which was then added to animal feed. This application prevented some of the food waste from these operations from entering waterways (USDA, 1969).

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)).

Lignin sulfonates are intended to be used as chelating agents for plant nutrients, dust suppressants, and emulsifiers. By virtue of their intended use, chemical interactions of lignin sulfonates with other substances would be expected. However, lignin sulfonates are generally nonreactive by nature. When used as emulsifiers, lignin sulfonates keep chemical mixtures dispersed in solution by limiting interaction between the two constituents of the mixture (Gundersen and Sjoblom, 1999). When lignin sulfonates come into contact with small soil particles through their use as dust suppressants or chelating agents, the soil particles are adsorbed to the lignin sulfonate due to the presence of polar and non-polar areas on the surface of the lignin molecule. These interactions do not generally result in chemical change but are mostly limited to a physical binding and adsorption. The exception to this is the corrosion of aluminum and its alloys by lignin sulfonates when the material is used as a dust suppressant. This reactivity is of concern due to the prevalence of aluminum or alloy wheels, which can be corroded by the lignin sulfonate as cars with this type of wheel drive over treated roads. Mixing the lignin sulfonate with calcium carbonate in slurry neutralizes the acidic lignin sulfonate and decreases the reaction with aluminum (CPWA, 2005).

Information on environmental or human health effects from chemical interactions with lignin sulfonate was not available. As a chelating agent, lignin sulfonates could serve to reduce environmental health effects and potential toxicity to humans from exposure to the free metal ions (Garcia-Valls et al., 2001). The biodegradability and relatively inexpensive nature of the lignin sulfonates were cited as factors supporting their use in remediation (see Specific Uses and Historic Use sections and the response to Evaluation Question #6).

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)).

Lignin sulfonates break down by physical or microbiological processes, but may persist in the soil up to one year. Lignin sulfonates are unlikely to accumulate in soil unless they are applied very frequently. Breakdown of lignin sulfonate occurs in part because lignin sulfonate is used as a carbon source by a variety of wood-decaying microorganisms. It is therefore likely that large amounts of lignin sulfonate applied to soils could stimulate soil microbial activity.

When lignin sulfonate decomposes in soil, sulfates, sulfonic acid groups, and CO_2 are liberated (Selin et al., 1975). The breakdown of a large amount of lignin sulfonate in the soil (resulting in the release of additional CO_2) could acidify the soil (CO_2 forms carbonic acid in the presence of water). Changes in pH due to the addition of large amounts lignin sulfonate could adversely affect plants and soil organisms, but these effects have not been quantified in the published literature.

Lignin sulfonate, usually as ammonium lignin sulfonate, is deliberately applied to soils when formulated as part of a plant micronutrient chelate. Micronutrient chelates, as described in the Specific Uses section, are large organic molecules used to envelop trace nutrient ions in a bound, but available form that is capable of providing nutrients to the plant while keeping the nutrient ions from forming insoluble complexes with other molecules in the soil (Jones and Jacobsen, 2009). Baicor, Inc. markets a product containing lignin sulfonates (chemical species not identified) called Plant Stimulator™ "Buffer." The manufacturer claims that this product is also intended to stabilize soils, but does not describe how the product does this or what "stabilize soils" specifically means (Baicor, 2011).

When lignin sulfonates are discharged to waterways, their decomposition removes dissolved oxygen from water. The lack of dissolved oxygen is harmful to aquatic organisms and, depending on the amount of lignin sulfonates that is discharged, can have a negative impact on aquatic organisms to varying degrees. Lignosulfonates are corrosive to aluminum and aluminum alloys in the absence of calcium carbonate. If the corrosion of aluminum or its alloys occurs as a result of lignosulfonate application to roadways, then contamination of nearby waterways with the corrosion products could result. If the lignosulfonate is applied with calcium carbonate in slurry, the effect is neutralized (CPWA, 2005).

<u>Evaluation Question #9:</u> Discuss and summarize findings on whether 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 and #6, lignin sulfonates used as dust suppressants or in chelates applied as plant nutrients to the soil may contaminate waterways via runoff following a rain event. When used as a flotation aid for dump tanks in pear processing, lignin sulfonates may be discharged to waterways due to improper disposal of the dump water (normal disposal would require treatment of the processing water before disposal). Accidental spills of lignin sulfonate may also result in contamination of waterways. Lignin sulfonates readily dissolve in water (forming acids) and may decrease the pH of waters they contaminate. The severity of this effect will depend on the amount discharged and the characteristics of the receiving water body. Due to their high BOD during decomposition, lignosulfonates will remove dissolved oxygen from waterways in amounts that may adversely affect aquatic organisms such as fish or aquatic invertebrates (CPWA, 2005).

As discussed above for Evaluation Question #8, lignin sulfonates decompose by physical or microbiological processes, but may persist in the soil in varying amounts at up to one year. However, significant amounts of lignin sulfonates are unlikely to accumulate in agricultural soils unless they are applied frequently.

Lignin sulfonate may be applied to control road dust. If these applications are frequent and are made during very dry periods, it may lead to an accumulation of lignin sulfonates in the road bed. Runoff flows along the ground surface could transfer the accumulated lignin sulfonate to nearby terrestrial systems or waterways. Large amounts of lignin sulfonates in agricultural soils could cause a decrease in pH (due to decomposition of lignin sulfonate, release of carbon dioxide and sulfur dioxide, and formation of acids) (see Evaluation Question #8). The acidification of the soil could adversely affect crops and soil microorganisms depending on the extent of acidification.

<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)).

The U.S. EPA issued an exemption from the requirement of a tolerance for lignin sulfonates when they are used as inert ingredients pre- and post-harvest in agricultural production. This exemption is based on the conclusion that there is a "…reasonable certainty that no harm will result…" to the general public, infants, and children from aggregate exposures (includes all dietary, drinking water, and non-occupational exposures) to lignosulfonates , as defined by the Federal Food, Drug, and Cosmetic Act (FFDCA) and the Food Quality Protection Act of 1996 (FQPA) (U.S. EPA, 2011a; Federal Register, 2005).

Evaluation Question #11: 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)).

Pear Flotation: No information was available on natural substances that may be used in place of the petitioned substance for pear flotation. Information was available on allowed synthetic alternatives to the petitioned substance, as summarized below.

As discussed in the Action of the Substance section, materials used to increase the specific gravity of dump water and provide flotation for pear include sodium silicate, sodium sulfate and sodium carbonate (Sugar and Spotts, 1989). Sodium silicate is an allowed synthetic substance for organic production that can be used (with restrictions) as a floating agent in postharvest handling of fruit (NOSB, 1995). Sodium sulfate is allowed for use in organic agriculture, but only as a livestock feed ingredient or in livestock healthcare (OMRI, 2010). Sodium carbonate is allowed for use in organic agriculture for processing non-agricultural ingredients and processing aids, as a crop fertilizer and soil amendment, and as a livestock feed ingredient (OMRI, 2010). There are no fruit processing or flotation uses described for sodium carbonate.

According to a survey from 1998 of pear packers in the western U.S., about 70 percent of packing houses used a form of lignin sulfonate for pear flotation (Sugar, 2002). However, a major source of lignin sulfonate in the Pacific Northwest closed prior to 2001, forcing growers to evaluate other alternatives for flotation (Sugar, 2002). Two new products were evaluated in 2001 by researchers at Oregon State University—K-Float (potassium carbonate) and Xeda F (potassium phosphate and potassium pyrophosphate)—along with sodium carbonate, calcium chloride, and sodium sulfate for their use in pear flotation. These products were evaluated at the Southern Oregon Research and Extension Center in Medford, OR, and the findings were reported at the Washington Tree Fruit Postharvest Conference on March 12th and 13th, 2002, in Yakima, WA. All tested products performed in a manner similar to lignin sulfonate to raise the density of water in dump tank solutions and allow pears to float for easier and less-damaging processing. When used in combination with Steri-Seal (an antimicrobial agent) the "relatively low" pH solutions containing Xeda F, calcium chloride, and sodium sulfate were more likely to cause fruit burn than the "relatively high" pH solutions including lignin sulfonate, sodium carbonate, and K-Float (Sugar, 2002). Fruit burn is caused in part by the increased availability of phenol that occurs at lower pH. For higher pH solutions, more Steri-Seal had to be added to dump tanks to prevent fruit infection (Sugar, 2002). In practice, multiple materials may be mixed at varying percentages in order to achieve the desired decrease in fruit injury and infection rates (Sugar, 2002). In these tests, a mixture of Xeda F with Steri-Seal disinfectant at 1percent provided the lowest gray mold infection rate (12 percent). However, all of the alternate treatments caused some degree of fruit injury at increased dump tank temperature. The exception to the rule was lignin sulfonate, which was found to lower pH levels, but also have a "safening" property for phenol injury at a low pH (Sugar, 2002).

Dust Suppression: Magnesium chloride and calcium chloride from nonsynthetic sources are allowed for use as a dust suppressant under certain circumstances (NOSB, 1995). Magnesium chloride from synthetic sources is allowed for use in organic agriculture for dust suppression only if it is derived from seawater (NOSB, 1995). Synthetic calcium chloride is allowed for use only as a livestock feed ingredient or in livestock healthcare (NOSB, 1995). "Plant Extracts" are listed in the NOP rule (205.105), but no dust-suppressant plant extract products were identified.

Chelating Agent: Nonsynthetic amino acids and nonsynthetic citric acid are allowed for use as chelating agents in organic agriculture (NOSB, 1995). Amino acids are considered nonsynthetic if they are produced by plants, animals, and microorganisms that have not been genetically-modified or if they are extracted or isolated by hydrolysis or by physical or other nonchemical means (NOSB, 1995).

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

Pear Flotation: Pear damage can occur throughout the harvest process, but one of the main sources of damage is when the pears are dumped from bins during rapid unloading. Dry dumps from harvest bins to packing bins can cause the most damage, whereas wet dumps (from a dry bin into a water-filled bin) decrease the potential for fruit injury. Wet dumps also allow pears to more easily move onto conveyors where they are inspected and packed. Due to the high density of pears, some are heavier than water. Flotation salts, including lignin sulfonates, are sometimes added to increase dump water density and allow the pears to float, thus reducing the chance for injury and increasing packing efficiency—a process called an immersion dump. The fruit is then circulated in the dump water using a pump, which floats the fruit to an elevator where it is rinsed and moved to a conveyor for packaging. The flotation salts could be left out of the process and non-immersion water dumps could be used. To minimize damage in non-immersion dumps from fruit-to-fruit injury, more time is required to allow fruit to move onto conveyors before additional fruit is dumped. Additional steps to reduce fruit damage have also been proposed which include using padded picking containers or plastic-lined wooden picking bins to reduce scuffing (Agar and Mitcham, 2000).

Dust Suppression: Alternate methods of dust suppression from best management practices include: vegetative cover (for non-traffic areas); mulch (including gravel mulch); sprinkling with water; spray-on adhesives (including anionic asphalt emulsion, resin in water, and latex emulsion); applications of stone or gravel to disturbed roads; barriers to control air currents; or surface roughening at angles perpendicular to prevailing winds (U.S. EPA, 2006; Idaho DEQ, 2005). Most of these methods (with the exception of adhesive applications and water sprays) do not involve applications similar to those used for lignin sulfonate, but are physical manipulations of the landscape. Cost, available resources, level of control, and the extent of the dust problem are factors that may affect the choice of dust control measures (U.S. EPA, 2006).

Researchers at Colorado State University evaluated three dust suppressants—calcium lignosulfonate, magnesium chloride, and calcium chloride—for their effectiveness in reducing dust emissions from unpaved roads (Sanders and Addo, 1993). Preliminary data analysis indicated that all suppressants reduced the dust emitted compared to untreated roads (Sanders and Addo, 1993). Final data (Sanders and Addo, 1993) showed that the aggregate loss of road height after one year was 5.18, 5.80, and 7.01 mm for roads treated with magnesium chloride, calcium lignosulfonate, and calcium chloride, respectively (Sanders and Addo, 2008). The untreated road showed an aggregate loss of 15.55 mm after one year.

Micronutrient Fertilizer Chelates: In addition to the use of allowed nonsynthetic chelates, soil fertility can be managed in other ways. Naturally-occurring chelates in the soil include humates, fulvates, and organic root exudates. Fulvates and humates are found naturally in most soils as the result of the decomposition of organic matter. Management practices, including no-till farming or manure applications, can increase organic matter in the soil and thereby increase the rate of naturally-occurring chelates (Jones and Jacobsen, 2009)

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APPENDIX B:

NOSB 2013 Technical Evaluation Report - Lignin sulfonates

Lignin Sulfonate

Aquaculture – Aquatic Animals

Identification of Petitioned Substance

Chemical Name:
Lignin sulfonate

Other Names:
Lignosulfonate
Lignosulfuric acid
Lignosulfonic acid
LST 7
Ligninsulfonic acid
Poly(lignosulfonic acid)
Protectol W
Sulfite lignin
(NLM, 2013a)

There are also various salts of lignin sulfonate listed in the CAS Numbers section.

Trade Names:
Lignosite® – Georgia-Pacific (Georgia-Pacific West, Inc., 2000)
BorrePlex – LignoTech USA, Inc. (OMRI, 2013)
Phyto-Plus® Plant Stimulator – Baicor L.C. (OMRI, 2013)
SHADOW – LignoTech USA, Inc. (OMRI, 2013)
Orzan – ITT Rayonnier (Sugar and Spotts, 1986)

CAS Numbers:
8062-15-5 (lignin sulfonic acid)

Lignosulfonate salts:
8061-51-6 (lignin sulfonic acid, sodium salt)
9009-75-0 (sodium lignosulfonate)
8061-54-9 (magnesium lignosulfonate)
8061-53-8 (ammonium lignosulfonate)
8061-52-7 (calcium lignosulfonate)
(U.S. EPA, 2010a)

Other Codes:
705707 (USEPA PC Code [U.S. EPA 2010b])
160226 (EPA Reference ID)
705705, 705708–705714 (U.S. EPA PC Code [U.S. EPA, 2010b], various lignosulfonate salts)
1522 (CODEX Alimentarius Commission INS Number, calcium lignosulfonate)

Summary of Petitioned Use

The petitioner is requesting the addition of lignin sulfonate, a synthetic substance, to the National List of Allowed and Prohibited Substances (hereafter referred to as the National List) for use as a synthetic substance allowed for use in organic aquatic animal production. Lignin sulfonate currently is allowed for use as a synthetic substance in organic crop production as a plant or soil amendment (chelating agent) and as a dust suppressant (7 CFR 205.601[j][4]), or as a floating agent in postharvest handling (7 CFR 205.601[l][1]).

Characterization of Petitioned Substance

Composition of the Substance:

Lignin is a constituent of woody plants that functions as a strengthening element. Lignin sulfonate is a derivative of lignin, where the lignin has been sulfonated in a wood pulping process (Zhor and Bremner, 1999). Lignin sulfonate has the chemical formula $C_{20}H_{26}O_{10}S_2$ (NLM, 2013b) and its structure is presented in Figure 1. However, lignin sulfonate may be composed of a variety of sulfonated aromatic alcohols which make up lignin polymers, including *p*-coumaryl alcohol, sinapyl alcohol, and coniferyl alcohol (FAO, 2008). The lignin molecule is complex and not well understood in spite of its prevalence (Pure Lignin, 2010). The sulfonate complex may be in association with calcium, magnesium, ammonium, or sodium (U.S. EPA, 2010b).

The National List identifies lignin sulfonate as a synthetic substance allowed for use in organic crop production (7 CFR 205.601). Because the lignin sulfonate molecule is negatively charged, it typically complexes with various cations to form lignin sulfonate salts. Four specific lignin sulfonate salts are included in the Generic Materials

List published by the Organic Materials Review Institute (OMRI): sodium lignosulfonate, magnesium lignosulfonate, ammonium lignosulfonate, and calcium lignosulfonate (OMRI, 2013). Although these salts are not specifically named on the National List, this Technical Report provides relevant information about them when available.

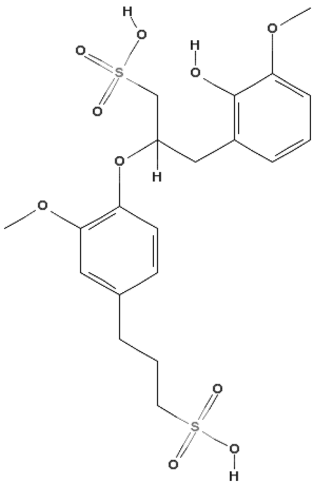

Figure 1. Chemical Structure of Lignin Sulfonic Acid, CAS 8062-15-5 (NLM, 2013b)

Source or Origin of the Substance:

Lignin exists naturally in all woody plants and is integrated into the plant cell wall, functioning as a structural and strengthening component. Lignin sulfonates are produced from lignin in the process of sulfite chemical pulping. This process involves cooking softwood chips under pressure in sulfur dioxide-containing cooking liquors. Sulfonated lignin is collected as a liquid byproduct in the spent liquor when the pulping process is complete, and the pulp is used for paper production. The lignin sulfonates that result are further purified through fermentation to remove excess sugars, and the resulting liquid is heated to remove alcohol resulting from fermentation (Zhor and Bremner, 1999; Westvaco Corp., 1987; U.S. EPA, 1990; Gundersen and Sjoblom, 1999).

Properties of the Substance:

A molecular weight of 490.5 g/mol has been reported for lignin sulfonate (NLM, 2013b). Other reports on the lignin sulfonates as a group state that they may have molecular weights ranging from 1,000 to 20,000 daltons or higher (up to 100,000 daltons in some cases) depending on their composition (Zhor and Bremner, 1999; Hawley, 1981). Weight-average molecular weights of calcium lignosulfonate are reported to range from 40,000 to 65,000 (unitless). Calcium lignosulfonate is soluble in water and insoluble in organic solvents (FAO, 2008).

Other physical and chemical properties of lignin sulfonate are presented in Table 1. The properties presented in Table 1 describe lignin sulfonate generally, unless a specific salt is otherwise indicated.

Specific Uses of the Substance:

The specific petitioned use of lignin sulfonate is as an animal feed additive, specifically a non-nutritive feed binder for use in aquaculture. In general, feed binders are added to fish feed pellets or particles to keep the feed whole during transport and handling and to maintain stability of the feed in water prior to consumption by the fish (Gatlin, 2010; Lende, 2013). Lignin sulfonate used as a binder for feed pellets allows for additional steam to be used during the manufacture of wet feed pellets because of its binding capacity and reduces the amount of fine particle debris leaving the pellets (Gatlin, 2010; Lende, 2013). Lignin sulfonate is typically added at 1–2% of the total pellet mass and at levels up to 4% of the dry weight of the pellets (Lende, 2013).

Table 1. Chemical Properties of Lignin Sulfonate

Chemical or Physical Property	Value
Color	Light tan to dark brown* ‡ † (CAMEO, Undated-a; CAMEO, Undated-b)
Physical State	Solid (powder) (Hawley, 1981)
Odor	Odorless (CAMEO, Undated-a)
Melting Point	Decomposes at >200°C (>392°F) (Hawley, 1981)
Boiling Point	Exists in a solid state
Solubility	Soluble in water† (FAO, 2008)
Stability	Soil half-life up to one year depending on chemical species and soil flora* † (Selin et al., 1975)
Reactivity	Lignin sulfonates are corrosive to aluminum and aluminum alloys in the absence of calcium carbonate (CPWA, 2005)
Oxidizing or Reduction Action	React as acids to neutralize bases. Usually do not react as reducing or oxidizing agents (CAMEO, Undated-a)‡
Flammability/Flame Extension	Flash point data not available although probably combustible (CAMEO, Undated-a)‡
Explodability	Dust explosions may occur if fine particles are mixed with air in the presence of an ignition source. Ignition temperature is approximately 250–300°C (482–572°F)* (Georgia-Pacific West, Inc., 2000)

*Sodium lignosulfonate
‡Ammonium lignosulfonate
†Calcium lignosulfonate

Lignin sulfonate is used in organic crop production as a plant or soil amendment (dust suppressant, chelating agent) and as a floating agent for postharvest handling of products (e.g., pears). Lignin sulfonate acts as a dust suppressant due to its large size and affinity for binding with other polar and nonpolar compounds. The smaller dust compounds adsorb to the lignin sulfonate and form a larger, heavier complex that is not as friable, which suppresses the dust (CWPA, 2005).

Chelating agents are large, organic molecules that are used to envelop highly-reactive trace metal ions. Lignin sulfonates can be used for the complexation of metal ions for the purpose of environmental remediation of heavy metals. Garcia-Valls et al. (2001) cited the biodegradability and relatively inexpensive nature of the lignin sulfonates as factors supporting their use in remediation. Lignin sulfonates have also been used in bioremediation at dairy operation facilities and meat and seafood canneries. Lignin sulfonates were applied to waste streams at the facilities to help remove dairy and seafood waste. The lignin sulfonates formed complexes with the waste materials, which then precipitated out of wash solutions. This process allowed for diversion of some food waste from waterways. The resulting food waste/lignin sulfonate complex was then used in animal feed (USDA, 1969). Lignin sulfonate is also used as a chelating agent to bind soil amendments (e.g., nutrients such as sulfate, phosphorus, calcium, and nitrogen; and biologically relevant metals including copper, iron, manganese, zinc, and others (7 CFR 205.601(j)(6)) for slow release (USDA, 1969).

When used as a floating agent, lignin sulfonate is added to dump water for fruit processing to increase the density of the water. Dump water is used to fill containers that receive fruit; the fruit is "dumped" into totes containing the water to limit damage during processing. This is necessary for fruits such as pears that may be heavier than water. Increasing the density of the dump water with lignin sulfonate allows the pears to float and, therefore, the pears are less likely to be damaged during processing (Agar and Mitcham, 2000).

Calcium lignosulfonate may be used as an inert ingredient or adjuvant (mixing agent/sticking aid) in pesticide products under 21 CFR §172.715, except for those exempt under Section 25(b) of the Federal

Insecticide, Fungicide, and Rodenticide Act (FIFRA)[1] (OMRI, 2013). Calcium lignosulfonate is also used as an encapsulating agent or carrier for fat-soluble carotenoids, vitamins, and other functional ingredients in foods such as fruit-based beverages, hard candies, vitamin drinks, and dairy products (Toledo and Kuznesof, 2008). As discussed in the Composition of the Substance section, other lignin sulfonate salts exist (U.S. EPA, 2010b) and are included on the OMRI Generic Materials List (OMRI, 2013), but little specific information is available about them.

Approved Legal Uses of the Substance:

Lignin sulfonate is currently included on the National List as a synthetic substance allowed for use in organic production (7 CFR 205.601). Lignin sulfonate may be used in organic crop production as a plant or soil amendment (dust suppressant, chelating agent, or floatation agent) or as a floatation agent in postharvest handling (see 7 CFR 205.601[j][4] and 7 CFR 205.601[l][1]). The OMRI generic materials list includes the following lignin sulfonate salts: sodium lignosulfonate, magnesium lignosulfonate, ammonium lignosulfonate, and calcium lignosulfonate (OMRI, 2013). These lignosulfonate salts are not specifically identified on the National List.

Under 21 CFR 573.600(a) and (b), the FDA Food Additives Permitted in Feed and Drinking Water of Animals, lignin sulfonate (including the ammonium, calcium, magnesium, or sodium salts of lignin sulfonate) may be used in a liquid form (moisture not to exceed 50% by weight) or a dry form (moisture not to exceed 6% by weight) in animal feeds. As specified at 21 CFR 573.600(b), lignin sulfonate may be used in an amount calculated on a dry weight basis:

(1) As a pelleting aid in the liquid or dry form in an amount not to exceed 4 percent of the finished pellets.
(2) As a binding aid in the liquid form in the flaking of feed grains in an amount not to exceed 4 percent of the flaked grain.
(3) As a surfactant in molasses used in feeds, as a liquid lignin sulfonate, in an amount not to exceed 11 percent of the molasses.
(4) As a source of metabolizable energy, in the liquid or dry form, in an amount not to exceed 4 percent of the finished feed.

Calcium lignosulfonate (CAS No. 8061-52-7) and sodium lignosulfonate (CAS No. 8061-51-6) may be used as inert ingredients in pesticide products. These inert ingredients are on EPA's former inert ingredients list (List 4B) which, in combination with List 4A, is used as a reference for allowed inert ingredients in organic pesticide products. In 2006, EPA changed its classification system for inert ingredients, but lists 4A and 4B are still referenced by the USDA organic regulations. The NOP still allows inert ingredients on these lists to be used as inert ingredients in pesticide products unless the ingredients were removed following EPA reassessment. Calcium lignosulfonate and sodium lignosulfonate have not been removed from the EPA List 4B and are therefore allowed for use as inert ingredients in pesticide products (USDA, 2009; U.S. EPA, 2010).

According to OMRI, ammonium lignosulfonate is an allowed form of lignin sulfonate, with restrictions, for use as a nutrient chelate in organic fertilizer products. According to OMRI, formulated fertilizer products that contain ammonium lignosulfonate may not make nitrogen claims on the label and/or the contribution of ammonium lignosulfonate to the total nitrogen content of the formulated product must be less than 1% based on 7 CFR 205.601(j)(4), 7 CFR 205.601(l)(1), and OMRI, 2013 .

Lignin sulfonate is exempt from the requirement of a tolerance when used as an inert ingredient in pre- and post-harvest agricultural production and as an inert ingredient applied to animals(40 CFR 180.910, 40 CFR 180.930) . Tolerances are acceptable levels of pesticide residues on food products that are set by the U.S. EPA and enforced by the USDA and FDA. According to 40 CFR 180.900, "An exemption from a tolerance shall be granted when it appears that the total quantity of the pesticide chemical in or on all raw

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[1] FIFRA is the federal law that regulates pesticide products in the United States and is administered by the U.S. EPA.

agricultural commodities for which it is useful under conditions of use currently prevailing or proposed will involve no hazard to the public health."

Action of the Substance:

Lignin sulfonate and other feed binders are added to feed mixtures to improve the durability and water stability of the feed by binding or sticking the composite feed together (New, 1987). Lignin sulfonate is known to have chelating or sticking properties based on its use as a dust control agent, chelating agent, and mixing agent/sticking aid in pesticide products (OMRI, 2013). To make pelleted fish feed, a finely ground feed mixture containing proteins of various types, carbohydrates, fats, vitamins, and trace minerals is prepared (FAO, 1980). Lignin sulfonate is added to the mixture before the mixture is added to the conditioning chamber and steam is applied (Uniscope, 2007). When the pellet mixture is passed through the conditioning chamber, water is added at a rate of 4–6% by weight, usually as steam, which causes the lignin sulfonate to become soluble and form an adhesive coating (FAO, 1980; Gatlin, 2010; Uniscope, 2007). The steam may also gelatinize existing starches in the feed, which contributes to feed stability (Gatlin, 2010). The feed is compressed by the pellet mill and forced through holes in a ring-type die, and the pressure forces the lignin sulfonate further into the pellet (FAO, 1980; Uniscope, 2007).

Combinations of the Substance:

Lignin sulfonate is formulated into feed pellets where it is combined with proteins of various types, carbohydrates, fats, vitamins, and trace minerals. Two of the synthetic substances allowed for use in organic livestock production as identified in 7 CFR 205.603(d) are typically used in fish feed: trace minerals, used for enrichment or fortification when FDA approved; and vitamins, used for enrichment or fortification when FDA approved. Lignin sulfonate sold as a feed binder is not combined with other materials, but is intended for combination with the pellet mixtures (FAO, 1980; Gatlin, 2010).

Status

Historic Use:

Lignin sulfonate has been used in organic agricultural production as a dust suppressant, chelating agent for micro- and macronutrient fertilizer applications, floatation agent in pear production, and as an emulsifier and stabilizer for pesticide applications. A previous technical report for lignin sulfonate was created as part of the 1995 petition process to add lignin sulfonate to the National List (USDA, 1995). A second technical report was prepared in 2011 for the Sunset Review of lignin sulfonate as an allowed synthetic substance used as a floatation agent, chelating agent, or dust suppressant (USDA, 2011).

Lignin sulfonate has been investigated for its potential as a chelating agent in the environmental remediation of heavy metals and in the remediation of food processing wastes (Garcia-Valls et al., 2001; USDA, 1969). Lignin sulfonate also has been used as an encapsulating agent for vitamins and other ingredients in food products (Toledo and Kuznesof, 2008).

Lignosulfonates have a variety of industrial applications. One of the main applications of lignosulfonates is in the concrete industry, where they may be used as dispersing agents and to delay the setting of concrete. In other industries, they may be used as additives in oil well drilling, dispersants for dyestuffs, cleaning agents, and as a partial substitute for phenol in the manufacture of adhesives. Sodium lignosulfonate is potentially useful in inhibiting corrosion and scale formation in recirculating cooling water systems (Ouyang et al., 2006).

Organic Foods Production Act, USDA Final Rule:

Lignin sulfonate is included within the scope of the Organic Foods Production Act of 1990 by implied inclusion in the group, "…an active synthetic ingredient in the following categories: copper and sulfur compounds…"

Lignin sulfonate is explicitly identified on the National List in 7 CFR Part 205, as follows:

- 205.601(j)(4) – Lignin sulfonate—chelating agent, dust suppressant.

- 205.601(l) – As floating agents in postharvest handling; (1) Lignin sulfonate

International:

Until 2008, lignin sulfonate was not allowed to be used in the production of certified organic products exported to Japan from the United States. In 2008, the Ministry of Agriculture, Forestry, and Fisheries (MAFF) in Japan lifted the ban of lignin sulfonate on organic crops imported to Japan. However, the products containing lignin sulfonate must be accompanied by an export certificate and must be imported by a JAS-certified importer (USDA, 2009).

The International Federation of Organic Agriculture Movements (IFOAM) includes calcium lignosulfonate on its "Indicative List of Substances for Organic Production and Processing." No other lignin sulfonates are included (IFOAM, 2008). As of 2009, calcium lignosulfonate is allowed by the CODEX Alimentarius Commission as a food additive, and the compound has been assigned INS Number 1522 (Codex Alimentarius Commission, 2010).

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). Lignin sulfonate is listed by inference as part of the group, "copper and sulfur compounds" in the OFPA, Section 2118 (c)(1)(B)(i).

(B). Lignin sulfonate is a synthetic inert ingredient that is not classified by EPA as an inert of toxicological concern. Lignin sulfonate (and the lignosulfonate salts) are exempt from the requirement of a tolerance under 40 CFR parts 180.910 and 180.930.

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)).

Lignin sulfonates are produced from the process of sulfite chemical pulping. Sulfite pulping involves cooking softwood chips under pressure in sulfur dioxide-containing cooking liquors. When the cooking process is complete, sulfonated lignin is collected as a liquid byproduct in the spent liquor, while the pulp is used for paper production. The lignin sulfonates that result from the spent liquor of the sulfite pulping process must be further purified to remove excess sugars. This is done by fermentation of the liquor followed by heating to remove the alcohol generated by fermentation. The resulting lignin sulfonate polymers can have high molecular weights ranging from less than 1,000 to more than 100,000 daltons (Zhor and Bremner, 1999; Westvaco Corp., 1987).

Lignin sulfonates may also be obtained from the Kraft pulping process; these are referred to as Kraft lignins. Kraft pulping is similar to sulfite pulping, but involves treating the wood at high temperature and pressure in a water solution containing sodium sulfide and sodium hydroxide. This process dissolves lignin into a soluble salt which dissolves in the pulping liquor. The lignin is removed by precipitation from the liquor using carbon dioxide (CO_2). The Kraft lignins must then be sulfonated after extraction by a reaction of the material with bisulfate or a sulfite compound (Gundersen and Sjoblom, 1999; U.S. EPA, 1990).

A third pulping process, acid sulfite pulping, is similar to Kraft pulping, but different chemicals are used. Sulfurous acid, used in place of sodium hydroxide, is combined with sodium, magnesium, calcium, or ammonium bisulfite. After the cooking is complete, the pulp is separated from the spent liquor, which may then be treated to obtain various chemical materials (U.S. EPA, 1990).

<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)).

Lignin exists naturally in all woody plants as a structural and strengthening component. Because lignin is integrated into the plant cell wall, there are no natural processes that liberate lignin other than natural decomposition of wood by microorganisms. Lignin sulfonates are produced from the application of pressure and heat to wood in the presence of sulfur dioxide or by the addition of alkali and various acids and sulfates, as described for Evaluation Question #2. This process adds the sulfonate moiety (part of a molecule) to the lignin, thus modifying it chemically, and the sulfonate moiety remains in the finished product. Purification of lignin sulfonate obtained from sulfite pulping is accomplished through fermentation to remove excess sugars. Although fermentation is a natural process, the heating of wood pulp under high pressure with the addition of acids is not a naturally-occurring process (U.S. EPA, 1990; Gundersen and Sjoblom, 1999).

Lignin produced from the Kraft pulping process, as described in the response to Evaluation Question #2, is removed from the pulping liquor using CO_2 and is then sulfonated after extraction. Sulfonation is carried out by reacting lignin with bisulfate or another sulfite compound, which remains as part of the resulting lignin sulfonate product (Gundersen and Sjoblom, 1999; U.S. EPA, 1990). Acid sulfite pulping is similar to Kraft pulping, but sulfurous acid is used in combination with sodium, magnesium, calcium, or ammonium bisulfite, and the product is further treated to yield the remaining lignin sulfonate (U.S. EPA, 1990). These are not naturally-occurring processes, and the materials used in the processes are not naturally occurring. For all processes, the remaining chemical moiety attached to lignin is sulfonate, which does not naturally occur in the lignin of woody plants and is the only material created in processing that remains in the final product.

<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)).

Lignin sulfonates are used to modify feed for aquatic animals that are raised under controlled conditions. These controlled conditions can be generally described as open or closed aquaculture systems. In an open system, fish are raised in netted pens that are in direct hydraulic exchange with surrounding water bodies. Closed aquaculture systems are closed off or away from surface water bodies, at least directly, and utilize water recycling practices (Cottee and Petersan, 2009). Closed systems may be more sensitive to environmental impacts due to their much smaller size, but open systems can have broader to larger scale environmental systems. It is much easier to control the environmental impacts of closed systems compared with open systems, and long-term impacts to open systems may be more difficult to detect.

Lignosulfonates discharged into water bodies from open systems may cause foaming and discoloration. Due to their high biological oxygen demand (BOD) during breakdown in water, lignosulfonates will remove dissolved oxygen from waterways in amounts that may be harmful to aquatic organisms in both open and closed systems (CPWA, 2005). This may be of concern if high amounts of lignin sulfonate are used in feed, or if large amounts of feed go to waste in ponds or tanks used to raise fish. However, the maximum amount of lignin sulfonate typically used in feed is 4% by weight, and 10% of the feed is typically not eaten by the fish (Craig and Helfrich, 2002). For larger aquaculture systems, in which considerable amounts of feed must be distributed in tanks or ponds where fish are raised, this could lead to larger deposits of lignin sulfonate from uneaten feed. Fish waste and waste feed, which also has a high BOD upon decomposition, will be present at much higher levels in aquaculture systems than lignin sulfonate, especially in closed systems. Management of nutrient balances would likely be included in the regular maintenance of wastewater systems in aquaculture production as required by EPA (U.S. EPA, 2012a; U.S. EPA, 2006). Little additional information is available in the published literature on the degradation pathways for lignosulfonates in water, and no information was found on environmental accumulation or bioaccumulation of lignosulfonates.

The half-life of lignosulfonates in soil, as evidenced by the loss of sulfates or sulfonic acid groups, is up to one year. Soil microorganisms, enzymatic reactions, and ultraviolet (UV) radiation contribute to the breakdown of lignosulfonates. The structure of lignosulfonates may be altered by wood-rotting fungi, with polymerization being the main pathway, based on a decrease in phenolic hydroxyl groups (Selin et al., 1975). Laccase, an enzyme produced by fungi, increased degradation of lignosulfonates to low-molecular weight fractions under laboratory conditions (Cho et al., 2004). In addition to microbial decomposition, enzymatic oxidative reactions contribute to the early breakdown process of lignosulfonates. Light (UV radiation) also hastens the degradation of lignosulfonates by creating radicals capable of degrading the lignosulfonate molecular structure. This breakdown process yields lower molecular weight lignosulfonate fragments and CO_2. The CO_2 may account for 15–20%of the original organic carbon. As lignosulfonates degrade, they become more susceptible to further degradation by microbial populations. Due to the complex and heterogeneous structures of lignosulfonates, the breakdown products are complex and variable (Lauten et al., 2010). Lignin sulfonate is not used as a fuel source when it is broken down by microorganisms, but rather incorporated into biomass through biosynthesis which broadens the scope of potential reaction pathways (Lauten et al., 2010). Given that lignin is a naturally-occurring component of wood, once the sulfonic acid groups have been cleaved, the lignin that remains would likely be broken down in a manner very similar to that of rotting wood.

Evaluation Question #5: 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)).

Lignin sulfonates are soluble in water, and it is likely that long-term addition of feeds containing lignin sulfonate would increase their concentration in a given body of water, particularly in closed systems that are not regulated properly. Lignin sulfonate and its breakdown products have the potential to adversely affect environmental systems in several ways. Lignin sulfonate and its breakdown products may cause acute or chronic toxicity to fish that ingest the feed although toxicity has only been observed at doses much higher than would exist in feed (Weber and Ramesh, 2005, as cited in Munro and Baines, 2009). Decreased dissolved oxygen (as well as decreased pH) may result from lignin sulfonate decomposition in aquatic systems. Lower pH levels can increase the availability of some metals in aquatic systems, leading to higher exposures in fish.

One study on lignosulfonates has shown toxicity to fish. A 48-hour LC_{50} of 7,300 parts per million (ppm) was observed by Roald (1977) in rainbow trout (*Oncorynchus mykiss*). As lignosulfonates break down in water, they consume dissolved oxygen in the water due to their high BOD, which may adversely affect aquatic organisms through a decrease in available oxygen for respiration (CPWA, 2005; Jones and Mitchley, 2001). Lignin sulfonates readily dissolve in water (forming acids) and may decrease the pH of waters they contaminate. The severity of this effect will depend on the amount discharged and the characteristics of the receiving water body (CPWA, 2005).

Due to the acidifying potential of lignin sulfonate, large spills of lignin sulfonate in water may decrease pH. If those same bodies of water are contaminated with mercury or other metals, the mercury may be more likely to enter the aquatic food chain (Reddy et al., 1995; USGS, 2009). One study in guppies (*Poecilia reticulata*) showed that while lignosulfonate in aerobic sediments helped to bind mercury and make it less bioavailable, lignosulfonate in anaerobic sediments stimulated the methylation of mercury, a more toxic metabolite of mercury (Gillespie, 1972). Methylation of mercury is also increased by decreasing pH, and pH is lowered when large amounts of lignin sulfonates are in water bodies (CPWA, 2005; Jones and Mitchley, 2001). For these reasons, mercury in waterways used to raise fish may be more likely to be taken up by fish, potentially leading to adverse health effects and human consumption (USGS, 2009). Findings of methyl mercury concentrations in farmed fish are contradictory; some studies have observed no effects when fish are fed on formulated compound feeds, while others have observed elevated concentrations when fish are fed marine-based feeds, indicating that the feed type may play a role, as well (Schultz et al., 2012).

Sodium lignosulfonate is relatively low in toxicity based on results of tests in laboratory animals, including rats, rabbits, and guinea pigs (Luscombe and Nicholls, 1973; Marcus and Watts, 1974). However, high doses of sodium lignosulfonate have been found to cause adverse health effects in laboratory animals. Rats that were given drinking water containing purified sodium lignosulfonate at a 10 g/100 ml concentration for 16 weeks had skin lesions at the bases of their tails, decreased weight gain, increased leukocyte counts, and increased kidney, spleen, and liver weights (Luscombe and Nicholls, 1973). In a study with guinea pigs and rabbits administered sodium lignosulfonate at a 1% concentration for a two- to six-week period, a high percentage of the animals developed ulcerative colon disease (Marcus and Watts, 1974). A median lethal oral dose of greater than 40 g/kg has been reported for rats (Luscombe and Nicholls, 1973). This dose corresponds to the U.S. EPA Toxicity Category IV for oral exposure (greater than 5000 mg/kg), which is the lowest toxicity category (U.S. EPA, 2007).

Results of a 28-day oral toxicity study in which calcium lignosulfonate was incorporated into the diet of rats at target doses of 0, 500, 1500, or 4000 mg/kg body weight per day showed no observed adverse effects other than chronic inflammation of the rectum at the highest dose level (4000 mg/kg-day). The no-observed-adverse-effect level (NOAEL), the concentration below which no adverse effects were observed, from this study was identified as 1300 and 1350 mg/kg-day for males and females, respectively (Weber and Ramesh, 2005, as cited in Munro and Baines, 2009). By comparison, 4000 mg/kg-day is 4 parts per thousand, or roughly ten times higher than the highest concentration of lignin sulfonate used in fish feed, which is 4 parts per 100, or 4%.

In a 90-day study with Wistar rats dosed with calcium lignosulfonate in the diet at target doses of 0, 500, 1000, and 2000 mg/kg-day, the rats showed no adverse clinical signs or organ weight changes following complete pathological evaluations. Test results for primary immune response in the rats were normal. The only observed adverse effect was a dose-related increase in the incidence of histiocytosis (abnormal increase in the number of immune cells) of the mesenteric lymph nodes in male and female rats, with no observed histiocytosis in other lymph tissues. The Joint FAO/WHO Committee reviewed the finding of histiocytosis and concluded that it does not represent an adverse effect, based on findings with other compounds with similar properties (Munro and Baines, 2009).

No evidence of genotoxicity (the ability of a chemical to damage DNA or other genetic material) was found for calcium lignosulfonate in *Salmonella typhimurium* and *Escherichia coli* assays, and in a test for chromosomal aberration in Chinese hamster cells. No developmental effects were found in a study with calcium lignosulfonate and pregnant female Wistar rats. The no-observed-effect level (NOEL) for reproductive effects was identified as 1000 mg/kg-day, the highest dose tested (Thiel et al., 2006b, as cited in Munro and Baines, 2009).

As discussed in a previous technical report on lignin sulfonate (USDA, 2011), the petitioner for lignin sulfonate (Western Chemicals) addressed concerns with dioxin as a contaminant from the process of paper pulping. Dioxin is a highly-toxic contaminant that is considered a likely human carcinogen (U.S. EPA, 2010c). The petitioner noted that dioxins are generally associated with the Kraft pulping process and that dioxins are produced as part of pulp bleaching. The original petitioner for lignin sulfonate for crop production noted that the Georgia-Pacific Corp. generates its lignosulfonates using the bisulfite pulping process (USDA, 2011). The petitioner also explained that the sulfite liquor, which contains the lignosulfonates, is removed from the pulp before the bleaching process; thus, it is not likely that dioxins would be found in the lignosulfonates generated from this process (USDA, 2011). In addition, the petitioner reported that they had analyzed their lignosulfonate products for dioxins and furans and have not detected the contaminants in their lignosulfonate products above the level of detection (USDA, 2011).

Georgia-Pacific Lignosite® 100, 260, 431-H, and 458 have been classified as biodegradable, with a hazardous decomposition product of sulfur dioxide (SO_2), which can adversely affect the respiratory system (Ash and

Ash, 2004; U.S. EPA, 2011a). Selin et al. (1975) commented on the recalcitrant (resistant to degradation) nature of lignosulfonates, but also showed that many wood-decomposing microbes could break down lignosulfonates. Lignin sulfonates bind strongly to smaller particles in the soil or water. Once adsorbed to the soil, lignosulfonates will likely be degraded by soil microorganisms. Lignosulfonates may persist for six months to one year in the soil before they break down (CPWA, 2005; Selin et al., 1975).

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)).

Environmental concentrations of lignin sulfonate in aquaculture are a function of multiple factors, including feed decomposition, feeding rates, utilization efficiency of feed, water circulation and exchange in a closed or open system, and the fate of lignin sulfonate given local conditions and the management of the system (Craig and Helfrich, 2002; Gatlin, 2010; New, 1987). Additionally, the potential for environmental contamination varies by life cycle scenarios, including manufacture, use, misuse, and disposal (Gatlin, 2010). The potential for contamination will also vary depending on whether a closed or open aquaculture system is used (Cottee and Petersan, 2009).

Manufacture: Spent sulfite liquors from the paper pulping process contain lignin sulfonate. Before the widespread use of lignin sulfonates, these liquors were treated as waste from the sulfate pulping process and discarded or burned for energy recovery. Given that lignin sulfonate is recovered from waste products of the paper pulp industry after manufacture, the likelihood of environmental contamination from its manufacture is reduced. However, there is still the possibility that spills of effluent from paper pulping operations could contribute large amounts of lignin sulfonate to soils, nearby waterways, or environmentally-sensitive areas. The same possibility of spills exists in manufacturing facilities that produce feed pellets for aquatic organisms, where lignin sulfonate may be stored in bulk. As discussed in the responses to Evaluation Questions #4 and #5, large spills of lignin sulfonate could acidify soils or bodies of water, decrease the available oxygen in bodies of water, or make mercury contamination of fish more likely in already contaminated waterways.

Use: Lignin sulfonates used as feed binders will be deposited in water bodies or closed aquaculture systems based on their usage pattern in fish feed. If the lignin sulfonate binder works as petitioned, then the fish feed is unlikely to break down before the fish consume the feed. The maximum concentration of lignin sulfonate in feed is 4% (Lende, 2013) and a maximum of 50% of that amount will likely be available in aquatic systems based on assumptions of the amounts of food eaten and waste produced by fish (Craig and Helfrich, 2002). The primary concerns regarding lignin sulfonates in waterways are their high BOD upon decomposition and potential to acidify the aquatic environment. In closed systems, this change will only have internal effects on the system until the water is disposed. In open systems, lignin sulfonate would be available to circulate through the aquatic ecosystem, broadening the exposure area but decreasing levels through dilution. High BOD leads to removal of dissolved oxygen (DO) from the water (CPWA, 2005). DO is a very important water quality indicator, and low DO levels can trigger stress responses in fish (Francis-Floyd, 2012). In addition a decrease in pH, resulting from lignin sulfonate decomposition, may also cause stress in aquatic organisms and make metals such as mercury more bioavailable (Francis-Floyd, 2012; Gillespie, 1972).

Misuse: Misuse of lignin sulfonate feeds by overfeeding could result in higher loads of the feed and, therefore, larger amounts of lignin sulfonate deposited to bodies of water or tanks and ponds used to raise fish. Dry decomposition of lignin sulfonate can release SO_2, which is an eye and airway irritant although it is unclear if this occurs in aquatic systems (Sullivan and Krieger, 1992; Georgia-Pacific West, Inc., 2000). Excessive amounts of feed containing lignin sulfonate or spills of feed into bodies of water may have the same effects. Dust explosions may occur if finely-divided lignin sulfonate is mixed with air in the presence of an ignition source. Excessive accumulation of dust should be avoided to help prevent explosions (Georgia-Pacific West, Inc., 2000).

Disposal: Water from closed aquaculture systems containing lignin sulfonate may need to be processed in a treatment system before its disposal. Any discharge of solids such as uneaten feed, waste, or animal remains must be minimized according to EPA aquaculture regulations (U.S. EPA, 2012b). For open systems, wastewater discharge must be limited (U.S. EPA, 2012b). As described in a fruit processing manual where lignin sulfonate is used in the process water, the goal for treatment of these waters before disposal is a reduction in BOD to a level that does not impact aquatic life (McLellan and Padilla-Zakour, 2005). The U.S. EPA has published Aquatic Life Criteria for DO in salt water in coastal areas from Cape Cod, MA to Cape Hatteras, NC (U.S. EPA, 2000). The criteria state that DO cannot be below 5 mg/L for "long periods," the level at which larval stages of many marine fish and shellfish are harmed (U.S. EPA, 2000). Untreated water could adversely affect aquatic organisms by competing for DO or lowering pH.

Under the Clean Water Act (Section 402), aquaculture projects are required to obtain National Pollutant Discharge Elimination System (NPDES) permits. NPDES permits are used to track and control discharges into navigable waters and are meant to protect the waters' ability to support aquatic life or permit recreation (U.S. EPA, 2012b). This includes any discharges into a "defined managed water area which uses discharges of pollutants into that designated area for the maintenance or production of harvestable freshwater estuarine or marine plants or animals" (U.S. EPA, 2012a). In addition, any concentrated aquatic animal production facilities, which are considered direct dischargers, require an NPDES permit if they produce more than 9090 kg (about 20,000 lbs.) harvest weight of cold water fish or produce more than 100,000 pounds of warm water fish annually (U.S. EPA, 2012a). The permits must be reviewed to determine whether the discharge may impair the waters' ability to support aquatic life, and would be denied if they are found to impair aquatic life (U.S. EPA, 2012a).

In the case of spills or accidents involving lignin sulfonate from closed systems, the area should be washed with water to dilute the spill (Georgia-Pacific West, Inc., 2000). To the extent possible, care should be taken to ensure that wastewater with high levels of lignin sulfonate does not flow directly to water bodies from closed systems. For these types of spills, waste disposal methods include customary procedures for industrial waste treatment (Georgia-Pacific West, Inc., 2000). Spills or releases of lignin sulfonate are not subject to the reporting requirements of the Federal Superfund Amendments and Reauthorization Act (SARA) of 1986 (Georgia-Pacific West, Inc., 2000).

Other: Lignin sulfonates have been investigated for their potential role as chelating agents for the complexation of metal ions, including copper, magnesium, and mercury, for the purpose of environmental remediation. The biodegradability and relatively inexpensive nature of the lignin sulfonates were cited as factors that support their use in remediation (Garcia-Valls et al., 2001).

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)).

By virtue of their intended use, chemical interactions of lignin sulfonates with other substances such as components of fish feed (proteins, fats, carbohydrates, ash, phosphorous, water, and trace amounts of vitamins and minerals) would be expected (Craig and Helfrich, 2002). Lignin sulfonates are generally nonreactive by nature, as evidenced by their uses in dust suppressants and emulsifiers. When used as emulsifiers, lignin sulfonates keep chemical mixtures dispersed in solution by limiting interaction between the two constituents of the mixture (Gundersen and Sjoblom, 1999). When lignin sulfonates come into contact with small soil particles through their use as dust suppressants or chelating agents, the soil particles are adsorbed to the lignin sulfonate due to the presence of polar and non-polar areas on the surface of the lignin molecule. These interactions do not generally result in chemical change but are mostly limited to a physical binding and adsorption. The exception to this is the observed corrosion of aluminum and its alloys by lignin sulfonates when the material is used as a dust suppressant (CPWA, 2005). Alum (aluminum sulfate) is used in aquaculture applications to clear muddy ponds (Williams, 2000). As shown in road dust applications, mixing the lignin sulfonate with calcium carbonate in slurry neutralizes the acidic lignin sulfonate and decreases the reaction with aluminum (CPWA, 2005). It may be possible to prevent corrosion and acidification of the water with a similar treatment in aquaculture applications although no specific methods were found. Appropriate water testing is urged when using alum in aquaculture to prevent acidification of water (Williams, 2000).

Information on human health effects from chemical interactions with lignin sulfonate was not available. As a chelating agent, lignin sulfonates could serve to reduce environmental health effects and potential toxicity to humans from exposure to the free metal ions (Garcia-Valls et al., 2001). The biodegradability and relatively inexpensive nature of the lignin sulfonates were cited as factors supporting their use in remediation (see Specific Uses and Historic Use sections and the response to Evaluation Question #6).

__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)).

Aquaculture is performed in in either open or closed systems. In open systems, finfish are raised in netted pens that are in direct hydraulic exchange with surrounding water bodies. Open aquaculture systems could also be used for shellfish such as clams, oysters, or shrimp, which may use other methods for exclusion of the farmed fish from the environment. Closed systems are closed off or away from surface water bodies, at least directly, and utilize water recycling practices (Cottee and Petersan, 2009). In both systems, wasted feed and animal wastes are two outputs that may adversely affect the agro-ecosystem although the adverse effects of waste are not all attributable to lignin sulfonate. The majority of waste material from aquaculture waste is not lignin sulfonate based on the fact that the highest concentration in fish feed is 4% by weight. These wastes are rich in nutrients that may affect BOD much more than the lignin sulfate additive.

Open aquaculture systems are more likely than closed systems to affect the environment at large because the water used in those systems is in continuous direct exchange with the surrounding aquatic ecosystem without waste management. However, the impact on farmed fish in open systems may be lessened by dilution with the surrounding water body. There are restrictions in place for open systems, such as the requirement of an NPDES permit for certain operations such as aquaculture projects or concentrated aquatic animal production facilities (U.S. EPA, 2012a). Under the NPDES system, aquaculture projects are defined as open systems that use "discharges of pollutants into that designated area for the maintenance or production of harvestable freshwater estuarine or marine plants or animals" (U.S. EPA, 2012b). Concentrated aquatic animal production facilities meet the following criteria: They produce more than 9,090 kg (about 20,000 lbs.) harvest weight of cold water fish or produce more than 100,000 pounds of warm water fish annually (U.S. EPA, 2012b).

Regardless of the restrictions, impacts from open systems, including discharges of fish waste and feed waste, reduced DO, and decreased pH, may be more difficult to mitigate (Cottee and Petersan, 2009). Sediments high in nutrients resulting from deposition of open system waste may also decrease DO as they decompose and affect aquatic life in areas outside of the farming operation (Kutti et al., 2007). One report found that oxygen consumption in the sediment below a fish farm could be as much as 15 times higher than in natural areas (Iwama, 1991, as cited in Cottee and Petersan, 2009). The DO and pH impacts may be exacerbated by lignin sulfonate breakdown. The impacts from open systems may adversely affect wild fish and the surrounding ecosystems due to nutrient imbalances and the production of large amounts of waste (Cottee and Petersan, 2009). Due to the likely effects on sediments, bottom-feeding fish and benthic (living at the bottom of a water body) organisms in open systems may be most intensely affected, while effects on pelagic (open water) fish and other organisms that live in the water column may be less severe. It is important to note that while adverse effects on aquatic systems may result from aquaculture practices, the total impact on those systems from lignin sulfonate in pelleted fish feed would be relatively small compared with overall waste and feed waste. In addition, the use of lignin sulfonate as a feed pellet binder slows the decomposition of feed and might prevent some waste from entering aquatic ecosystems.

In closed aquaculture systems, animal waste may have an increased impact on the quality of water in the system due to reductions in DO levels, increases in carbon dioxide, and increases in levels of ammonia, nitrate, nitrite, and suspended solids (Cottee and Petersan, 2009). The use of lignin sulfonate in feed in those systems may lead to additional reductions in DO and decreases in pH. Fish respond to low levels of DO and decreased pH with a stress response, which may lead to infections of the blood and other tissues

(Cottee and Petersan, 2009). Disposal of wastewater from closed systems, if performed according to U.S. EPA guidelines for aquaculture and NPDES permit requirements, would not be expected to adversely impact the environment (U.S. EPA, 2012a; U.S. EPA, 2012b). U.S. EPA aquaculture guidelines encourage individuals to recycle aquaculture waste and to avoid the discharge of waste into U.S. waters generated by rinsing or washing of nets (U.S. EPA, 2006).

According to U.S. EPA guidelines for aquaculture NPDES permits, solid wastes from aquaculture production, including waste feed and fecal matter, are required to be captured from liquid wastewater and disposed (U.S. EPA, 2006). These solids might be disposed on land (e.g., as fertilizer, compost) or in evaporation ponds or reed drying beds (U.S. EPA, 2006). All of these methods aim to limit waste discharge and encourage recycling of nutrients in a manner that limits environmental impacts (U.S. EPA, 2006).

Although it is not likely, if wastewater is not disposed of properly and discharged to soils, it could have adverse effects. When lignin sulfonate decomposes in soil, sulfates, sulfonic acid groups, and CO_2 are liberated (Selin et al., 1975). The breakdown of a large amount of lignin sulfonate in the soil (resulting in the release of additional CO_2) could acidify the soil because CO_2 forms carbonic acid in the presence of water. These changes due to the addition of large amounts lignin sulfonate (which would be unlikely based on the low percentage of lignin sulfonate in fish feed) could adversely affect plants and soil organisms. These effects have not been quantified in the published literature. These impacts would not be of issue if the wastes are disposed of according to U.S. EPA regulations.

<u>Evaluation Question #9</u>: **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 the responses to Evaluation Questions #4 through #8, lignin sulfonates may contaminate waterways through buildup of waste feed over time in open systems or disposal of large amounts of water from closed aquaculture systems. Lignin sulfonates readily dissolve in water (forming acids) and decrease the pH of waters they contaminate. Contamination from improper disposal of aquaculture waste containing lignin sulfonate or accidental spills would lead to decreased DO in the waterways due to the high BOD of aquaculture wastes and lignin sulfonate. As discussed in the response to Evaluation Question #7, lignin sulfonate is a minor component of aquaculture waste but could still lead to decreased DO in aquaculture systems. Decreased DO and lower pH can adversely impact all aquatic life, as evidenced by increased stress responses in fish (CPWA, 2005; Francis-Floyd, 2012). Increased stress responses can lead to higher prevalence of diseases in both the farmed fish and any aquatic organisms in open systems.

The severity of effects on the aquatic environment due to lignin sulfonate in feed will vary depending on the amount discharged and the characteristics of the receiving water body. Lignin sulfonate used in open systems is more likely to adversely impact the environment, while closed systems may be managed in a way that limits environmental impacts. Certainly, the adverse impacts of aquaculture will exist regardless of whether lignin sulfonate is used as a pellet binder in aquatic feeds. The low concentration (4%) of lignin sulfonate in feed indicates that it will play a minor role in the overall environmental impact of aquaculture waste. Although it is likely low, the precise environmental impact of lignin sulfonate used in aquaculture has not been studied and is as yet unknown for both open and closed systems.

<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)).**

No data were found that indicate there would be direct adverse effects on human health from use of lignin sulfonate in the formulation of fish feed. The U.S. EPA issued an exemption from the requirement of a tolerance for lignin sulfonates when they are used as inert ingredients pre- and post-harvest in agricultural production under 40 CFR 180.910. This exemption is based on the conclusion that there is a "…reasonable certainty that no harm will result…" to the general public, infants, and children from aggregate exposures (includes all dietary, drinking water, and nonoccupational exposures) to lignosulfonates, as defined by the

Federal Food, Drug, and Cosmetic Act (FFDCA) and the Food Quality Protection Act of 1996 (FQPA) (U.S. EPA, 2011b). Although this is not a guideline based on aquaculture use, the "incorporation" of lignin sulfonate into fish that will become food likely retains a low level of concern. There is no published evidence of lignin sulfonate accumulating in fish that are fed pellets containing lignin sulfonate.

Evaluation Question #11: 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)).

Many substances are used as feed binders for increasing water stability of aquaculture feeds (New, 1987). Substances used to make feed more stable include: casein, gelatin, collagen, chitosan, guar gum, locust bean gum, agar, carrageenan, corn starch, tapioca starch, potato starch, wheat gluten, sodium alginate, hemicellulose, bentonite, banana waste, and (New, 1987). Chitosan, carageenan, and collagen have been evaluated as feed binders but are not commonly used (Lende, 2013). Some of the substances listed above may be available in organic forms, such as organic corn, tapioca, or potato starch; and some of the compounds listed may be used in organic handling (7 CFR 205.605 and 7 CFR 205.606) , such as bentonite, guar and locust bean gum.

The most widely used of these substances as feed binders are starches (corn, tapioca, or potato), bentonite, lignin sulfonate, and hemicellulose (Lende, 2013). Table 2 below shows the water stability of test pellets made with many different types of binders including rice dust, soybean flour, and corn solids in a standard feed formula. In this series of experiments in which a number of binders were tested (FAO, 1980), rice mill dusts (a starch from the milling of rice) had the longest solids retention time (i.e., the duration that feed pellets remain solid before breaking down) of all the binders tested.

Table 2. Water Stability of Test Pellets in a Standard Formula*

Test Pellet	Percentage of Solids Retained
5% gelatinized corn solids (dry)	85.0
5% bentonite	88.6
Control formula - unground	90.0
5% guar meal	90.2
5% gelatinized corn solids - wet	92.0
Control formula ground through 2 mm screen	93.0
5% rice mill dust, 75 microns diameter	93.0
5% soybean flour	94.0
5% lignin sulfonate	94.0
5% rice mill dust sifted through 180 microns	96.2
10% rice mill dust sifted through 180 microns	98.2
20% rice mill dust sifted through 180 microns	98.5

*Measured as percentage of solids retained on a screen after 10 minutes in quiet water (FAO, 1980).

Starches (from wheat, rice, or corn) are used as binders in aquatic feeds that are steam pelleted or extruded, where gelatinization of the starches by water and heat dissolves the starch granules and distributes the gelatinized starch to bind the pellet (Tucker and Robinson, 1990). For pellet feeds, depending on the temperature and pressure under which the pellets are produced, the starch may cause the pellets to float or sink, a characteristic that is set depending on the variety of aquatic livestock being fed (e.g., floating pellets are preferred for salmonids, sinking pellets are better for catfish) (Stickney, 2009). Due to the heat and pressure of the extrusion process, it is usually not necessary to add binders like lignin sulfonate to floating feeds that contain starch because the starch binds the feed sufficiently (Tucker and Robinson, 1990).

Pelletized feeds may require additional non-nutritive binders such as lignin sulfonate, bentonite, or cellulose to provide additional stability and decrease the amount of feed dust (Tucker and Robinson, 1990). Pregelatinized starches have been characterized as relatively expensive (Smiley, 2012), but starches and sugars are noted as some of the most economical sources of energy for fish diets (Craig and Helfrich, 2002).

Bentonite is a type of clay that is added to fish feed and consists mainly of colloidal aluminum silicate with varying amounts of iron, alkalies, and alkaline earths (21 CFR 184.1155[a]; FDA, 1977). Bentonite is added to compressed, dry fish feeds at no more than 2% as a binding agent and lubricant for feed pellet mills (Lende, 2013). Bentonite is naturally occurring and is used in the food industry to clarify liquids and as an ingredient in coatings and adhesives for food packaging (FDA, 1977). Bentonite is considered generally recognized as safe (GRAS) by the U.S. FDA (21 CFR 184.1155[c]). As shown in Table 2, bentonite had the shortest solids retention time with the exception of corn solids (FAO, 1980).

Another alternative to the use of lignin sulfonate in pelleted feeds is hemicellulose. Hemicellulose is a nondigestible starch that is used as a non-nutritive binder in steam pelleted feeds. Hemicellulose extract is allowed for use in animal feed if it meets the following conditions as specified in 21 CFR 573.520:

a) The additive is produced from the aqueous extract obtained by the treatment of wood with water at elevated temperatures (325 degrees-535 degrees F) and pressure (80 to 900 pounds per square inch) and contains primarily pentose and hexose sugars.

b) The additive may be used in a liquid or dry state with the liquid product containing not less than 55 percent carbohydrate and the dry product containing not less than 84 percent carbohydrate.

c) The additive is used as a source of metabolizable energy in animal feed in accordance with good manufacturing and feeding practices.

Table 3 provides a list of selected companies that manufacture feed binders or nonorganic fish feed using alternate binding materials.

Table 3. Selected Manufacturers of Feed Binders or Nonorganic Fish Feed with Alternate Binding Materials

Ingredient	Company	Address
Rice starch (premanufactured feed)	Wet Thumb Aquatics	52700 Base St., New Baltimore, MI 48047 www.wetthumbaquatics.com
Bentonite (for adding to feed)	Bentonite Performance Minerals, LLC	3000 N. Sam Houston Pkwy. East Houston, TX 77032 www.bentonite.com
Hemicellulose (premanufactured feed)	M-G Feed Inc.	P.O. Box 697 Weimar, TX 78962; m-ginc.com

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

Types of aquatic feed formulations include pellets, crumbles, and finely ground meals, and most contain no more than 10% moisture (Gatlin, 2010). Most diets are sold as dry products although some semi-moist diets are made for early life stages or carnivorous fish (Gatlin, 2010). Moist diets with moisture contents of 35% to 70% will always require a binder, whereas semi-moist feed with 25% to 35% moisture can be made into pellets by selecting feed ingredients that also act as binders, such as certain starches (Halver and Hardy, 2002). The use of starches to bind the pellets is an alternative to non-nutritive binders such as lignin sulfonate, and the types of starches may vary, but include rice, corn, wheat, tapioca, and potato starch (New, 1987). However, if nutritive binders are not included in the feed recipe, then non-nutritive binders must be used (Halver and Hardy, 2002).

Compression pelleting of feeds is the most common type of feed manufacture for sinking pellets, while cooking extrusion is the most common form for floating pellets, and is also very costly (Gatlin, 2010). In compression pelleting, starch gelatinizes during the preconditioning and pelletizing processes, which increases cohesion and durability of the pellets, which may preclude the need for additional binders (Gatlin, 2010). However, sometimes a pellet binder is still included to increase the durability of feed pellets (Gatlin, 2010). With the extrusion process, the feed is still heated during preconditioning, but it is then heated to a higher temperature at higher moisture content than with compression pelleting, causing the pellets to expand when they exit the extrusion barrel, reducing their density (Gatlin, 2010).

Water stability of feeds can be improved by using finely ground raw materials as well as die plates that produce smaller pellets (New, 1987). However, these techniques and others aimed at increasing feed water stability may considerably increase the cost of processing the feed (New, 1987). One report suggests that the need for extremely well-bound feed is up to the farmer. If the diet is consumed within a few minutes of feeding or if more frequent feeding can be accommodated, then the need for extremely well-bound feed may be decreased (New, 1987). New techniques are available for formulating feeds—including microbinding, microencapsulation, or microcoating—that may eliminate the need for some types of binders (Lovell, 1998).

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Appendix C

Technical Review of Sodium Carbonate Lignin by Khalil Jradi, PhD. Chemistry April 2019

Cascades

CASCADES CS+ INC.
Cascades Research and Development

471 Marie-Victorin Blvd.
Kingsey Falls (Quebec) Canada
J0A 1B0
Telephone: 819-363-5700
Fax: 819-363-5755

April 25, 2019

Request #:	**190429**
Billing #:	**A02120**
File:	**NOTR**

To : Lucie Zillinger
Consultant for Legnochem, Ontario

From : Khalil Jradi, PhD
Chemist,

c.c. : Denis Major, Benoit Dionne, Leon Marineau

Assistance for the Sodium Carbonate Lignin petition submitted by Legnochem

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I. ABSTRACT

At the Cascades Containerboard Packaging – Trenton mill, large quantities of **soda liquor** or “sodium carbonate liquor” are produced though the soda pulping process, and they represent significant value as beneficial co-product as compounds for materials applications. Among those, the soda liquor which contains sodium carbonate lignin (also known as sodium lignin) is currently used as a binder for the pelletization of mined minerals in order to supress dust (particulate matter) during spreading and handling. The pelletized minerals are then used as soil amendments for conventional crop production.

A petition has been submitted to the Canadian and US organic programs by Legnochem (prepared by consultant Lucie Zillinger) to have sodium carbonate lignin allowed for the same application for organic production and is currently under review by these regimes.

The petition asserts that sodium carbonate lignin is essentially equivalent to lignin sulfonates which are already allowed for organic crop production. To enable sodium lignin to be re-evaluated by OMRI as equivalent to lignin sulfonates, confirmation about

the chemical composition and the characteristics of the soda lignin must be provided. In this context, CS+ was requested to confirm the technical information presented by Lucie Zillinger about the sodium carbonate lignin in order to support the petitions submitted to the US NOP and the Canadian COR.

II. AIM

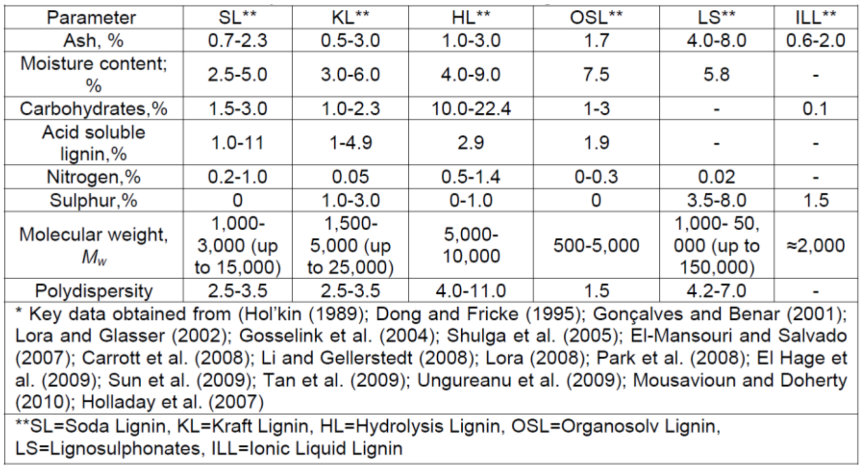
The aim of this work is to confirm and substantiate by subject expert technical review the information collected by the consultant of Legnochem about the sodium carbonate lignin in order to support the petitions submitted to NOP and COR.

III. REVIEW

1. *What are the main components in the soda process black liquor – e.g. lignin fragments, inorganic chemicals, hemicellulose, lignin complexed with hemicellulose, etc.*

According to the literature and the chemical analysis performed at the Research and Development Center of Cascades CS+ (**1,2,3,4**), the main components presents in the sodium carbonate liquor are: lignin fragments, hemicellulose (xylan and glucomannan, etc.), lignin-hemicellulose complexes, residual monosaccharides (resulting from the hydrolysis of hemicellulose/cellulose during the pulping process); resinous compounds of low molar masses, organic acids, and others extractives as well as inorganic compounds that come from soluble salts ions as Na_2CO_3, NaOH, and metal elements (principally Na, Zn, Mn, K, and others metals in the trace levels). The details about the inorganic composition are presented in the answer to the question N°3 (section III.3). Such composition could vary slightly depending on the type of wood used in the pulping process.

Table 1: Chemical composition of technical lignins (included soda lignin, kraft lignin, lignosulphonate, etc.) **(1).**



Parameter	SL**	KL**	HL**	OSL**	LS**	ILL**
Ash, %	0.7-2.3	0.5-3.0	1.0-3.0	1.7	4.0-8.0	0.6-2.0
Moisture content; %	2.5-5.0	3.0-6.0	4.0-9.0	7.5	5.8	-
Carbohydrates,%	1.5-3.0	1.0-2.3	10.0-22.4	1-3	-	0.1
Acid soluble lignin,%	1.0-11	1-4.9	2.9	1.9	-	-
Nitrogen,%	0.2-1.0	0.05	0.5-1.4	0-0.3	0.02	-
Sulphur,%	0	1.0-3.0	0-1.0	0	3.5-8.0	1.5
Molecular weight, M_w	1,000-3,000 (up to 15,000)	1,500-5,000 (up to 25,000)	5,000-10,000	500-5,000	1,000- 50,000 (up to 150,000)	≈2,000
Polydispersity	2.5-3.5	2.5-3.5	4.0-11.0	1.5	4.2-7.0	-

* Key data obtained from (Hol'kin (1989); Dong and Fricke (1995); Gonçalves and Benar (2001); Lora and Glasser (2002); Gosselink et al. (2004); Shulga et al. (2005); El-Mansouri and Salvado (2007); Carrott et al. (2008); Li and Gellerstedt (2008); Lora (2008); Park et al. (2008); El Hage et al. (2009); Sun et al. (2009); Tan et al. (2009); Ungureanu et al. (2009); Mousavioun and Doherty (2010); Holladay et al. (2007)

**SL=Soda Lignin, KL=Kraft Lignin, HL=Hydrolysis Lignin, OSL=Organosolv Lignin, LS=Lignosulphonates, ILL=Ionic Liquid Lignin

2. Confirm the entries in the Physical Properties Table Given Below:

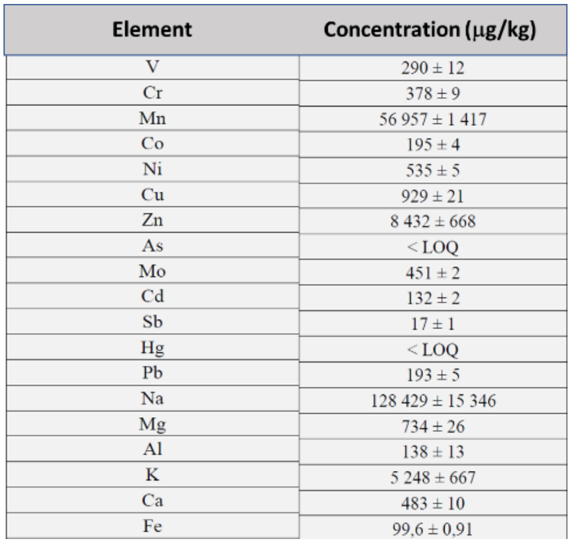
Table 2: Physical Property Table for Sodium Carbonate Lignin Liquor at 50% solids

Chemical or Physical Property	Value
Color	Dark brown liquid…. **OK**
Physical State	Viscous Liquid…. **OK**
Odor	Wood odor…. **OK**
Melting Point Deg C	-8 Deg C…. **OK**
Boiling Point	100 Deg C…. **OK (slightly higher than 100 °C)**
Solubility	Completely soluble…. **OK (the soda liquor is soluble in water, but the individual soda lignin is not soluble, off course depending the extraction method…)**
Stability	Very stable…. **OK**
Reactivity	Reacts mildly with acids due to small proportion of sodium carbonate, producing carbon dioxide. Mildly reactive to metals…. **OK**
Oxidizing or Reduction Action	Reacts as mild base to neutralized acids. Usually does not react as reducing or oxidizing agent… **OK**
Flammability/ Flame Extension	Flash point data not available although probably combustible.... **OK**
Explodability	Not available **(Heat of combustion of the soda liquor is about 13 MJ/kg)**
PH	7.0- 9.0 being most common.… OK

3. A brief discussion of the inorganic chemicals in the liquor - what are the main components present?

As discussed above (question N°1) and based on the chemical analysis performed at Cascades CS+ (Table 3), the main inorganic components present in our sodium carbonate liquor come from soluble salts ions such as Na_2CO_3, NaOH, and metal elements in trace levels (**5,6**).

Table 3: Analysis of chemical elements presents in the soda liquor by ICP/MS (**7**).



Element	Concentration (µg/kg)
V	290 ± 12
Cr	378 ± 9
Mn	56 957 ± 1 417
Co	195 ± 4
Ni	535 ± 5
Cu	929 ± 21
Zn	8 432 ± 668
As	< LOQ
Mo	451 ± 2
Cd	132 ± 2
Sb	17 ± 1
Hg	< LOQ
Pb	193 ± 5
Na	128 429 ± 15 346
Mg	734 ± 26
Al	138 ± 13
K	5 248 ± 667
Ca	483 ± 10
Fe	99,6 ± 0,91

By comparison, the sodium carbonate lignin is sulfur-free, and the inorganic salts (Na_2CO_3 and NaOH) are also present in the both soda, kraft and sulfite liquors. Moreover, since soda lignin is sulfur-free, this means the chemical composition of soda lignin is closer to that of native lignin in comparison with kraft lignin and lignosulphonate (**8,9**).

4. A discussion of how the main components of our liquor might compare to Kraft liquor or sodium sulfite pulping liquor. This is to support our assertion that most of what is in our liquor is also in these others.

Based on the literature, black liquor (in general) contains water, organic residues from pulping, and inorganic cooking chemicals.
In the case of kraft or sulfite liquor, the primary organic compounds are lignin, polysaccharides, carboxylic acids, and extractives, the main inorganic substances in black liquor are Na_2CO_3, Na_2SO_4, Na_2S, $Na_2S_2O_3$, NaOH and NaCl.

Typical content of spent liquor from various cooking conditions are listed in the tables 4 and 5.

Table 4: Typical composition of the recovered black liquor from various cooking condition (**10**).

	Content (% of dry solid)	
Components	Kraft liquor	Sulfite liquor
Lignin	39-54	55
Degraded carbohydrates	25-35	28
Extractives	3-5	4
Inorganic components	18-25	13

Table 5: Comparison of chemical content of the recovered black liquor from various cooking condition (**11**).

	Content (% of dry solid)		
Components	Kraft liquors[a]	Soda liquor[b]	Sulfite liquor[c]
Lignin	39-54	15-35	55*
Degraded carbohydrates	25-35	25-41	28
Extractives	3-5	n.a.	4
Inorganic components	18-25	n.a.	n.a.

* In form of lignosulfonates

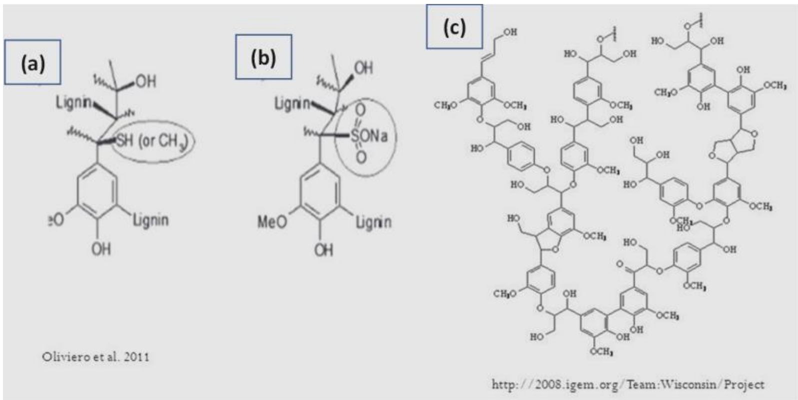
a (AFPA, 2003; Rojas et. al, 2006)

b (Feng et. al, 2001; Feng et. al, 2002; Mohd Ibrahim & Chuah, 2004; Sun et. al, 1999)

c (Sjostrom, 1993)

Comparing kraft and sulfite liquor with the soda liquor, it appears clearly that the chemical compounds of the soda liquor are also presents in the other liquors.

Based on the chemical structures of different lignins (Figure 1), we observe that the all aromatic cycles of lignin are clearly in phenolic hydroxyl and methoxy moieties.



Oliviero et al. 2011

http://2008.igem.org/Team:Wisconsin/Project

Figure 1: Structures of different lignins: (a) kraft lignin, (b) lignosulfonate and (c) soda lignin.

In conclusion, it can be shown that lignin fragments produced in the soda process are in fact also present in the kraft and sulfite liquors already accepted by the NOSB. However, the chemical groups (SO_3^-, SH, OH, COOH, etc.) contained in the structure of lignin fragments vary slightly depending on the type of wood used in the pulping process.

5. ***How sodium carbonate lignin black liquor is more benign than liquors from sulfate processes. For example, explain that the lignin is not modified in soda process liquor, etc.***

The soda ash process is considered a semi-chemical process and is very benign as it uses no sulfur or bleaching agents. Sodium Carbonate, the cooking chemical is also used for water softening. In the absence of any sulfur content, soda pulping leads to the production of sulfur-free lignin. It is reported in literature that lignin and lignin-carbohydrate complexes are less degraded after soda treatment than kraft treatment (**12**). In soda lignin, lignin-carbohydrate complexes (LCCs) consist of up to 34% of carbohydrates (meaning they are closer to their natural state) (**4**). Given that the soda lignin is much more like native lignin than lignosulfonate and kraft lignin, this characteristic provides new opportunity for soda lignin in different applications as adhesives (phenols resins) and it is a better choice for animal health and nutrition products compared to lignosulfonate and kraft lignin in term of toxicity (**13**).

When comparing the whole pulping cycle, the chemical recovery system of soda pulping is essentially the same as of kraft pulping. Whereas, soda pulping does not involve the use of sulfur compounds to facilitate delignification, thus the emission of total reduced sulfur (TRS) and the related odour problem associated with kraft pulping do not occur. Consequently, soda mills do not have to install the extensive TRS control system which is generally required by kraft mills to reduce the TRS emission (**14**).

6. ***What is the primary mode of action for the lignin compounds to have binding properties? Confirmation that these interactions of the lignin compound to minerals like gypsum and lime and rock phosphate do not generally result in chemical change but are mostly limited to a physical binding and adsorption.***

Y. Lu et al. (**15)** confirm in their research that sodium carbonate lignin has binding properties. They state that the alkaline nature of the soda pulping leads to the ionization of the phenolic hydroxyl (and possibly carboxyl) groups of the lignin which enhance the physical interaction of lignin fragments with minerals (through polar and non-polar interactions) which is known to have a positive impact on the pelletization mechanism.

In my professional opinion, in the desired application (pelletization of minerals), the very low amount of sodium carbonate lignin added in the medium (2 % w/w) could not alter the chemical structure of the minerals. The calcium ions in lime and gypsum do however promote the physical interactions between these minerals and lignin fragments via chelation. When the soda lignin (2%) comes into contact with the mineral particles (such as gypsum, lime and rock phosphate), the presence of calcium ions in gypsum and lime facilitate the formation of complexes of lignin-calcium where the calcium acts as a chelating agent with lignin fragments of the soda liquor. The interactions of calcium from the gypsum with lignin fragments (case of kraft lignin) contribute to the formation of Ca-lignin chelating complex after drying (**16**) and such complexes enhance the thermal stability of the mixture lignin-gypsum-lime (**17,18**).

Such interactions are the same in the case of the soda lignin in which the ionised hydroxyl groups of lignin formed by alkaline pulping (lignin–OH ⇒ lignin–O^-) form a complex with calcium ions and consequently, enhance their binding in the mineral matrix.

Following the alkaline treatment used in the soda pulping, the extracted lignin fragments (and their complexes with carbohydrates) contain a high amount of hydroxyl groups (polar groups) which help them to bind to the minerals particles and enhance their aggregation. Such interactions do not result in chemical change and are limited to physical binding and adsorption.

Research excerpts on binding mechanism and properties of sodium carbonate lignin:

The structure of lignin is complex, but today, the structural elements are quite well known. Due to its hydrophilic nature, the soda lignin system is sensitive to high clay content (**19**) which could promote physical interactions necessary for soil stabilization.

The utilisation of additives obtained from biofuel plants has been gaining research interest for their ability to improve aggregate stability. Works performed by Ceylan et al. (**20**), Zhang et al. (**21**), Canakci et al. (**22**), have investigated the use of sulfur-free lignin in improving the stability of road beds. Zhang et al. (**22**) also reported strength increases with 12% lignin content for a silty soil. These studies further showed that sulfur-free lignin have effective binding effects on soil particles and improved stability of soil (for example in road construction).

Specifically, lignin acts like a cementing material and binds all the soil particles together into a homogeneous mass (**23)**.

In mixtures of lignin fragments with mineral particles within soil, the soil particles are adsorbed onto the surface of the lignin through different physical interactions (hydrogen bonding, Van der Waals and electrostatic bonds, etc.) and such interactions are promoted by the presence of polar and non-polar areas on the surface of the lignin fragments. These interactions do not result in chemical change but are mostly limited to physical binding and adsorption.

Consideration of the solubility of lignin soda in water and its effect on the binding mechanism onto mineral particles:

It is known that the kraft lignin and soda lignin (both also known as alkali lignins) are not water soluble at pH 7 when compared to lignosulfonates. This could be due to the presence of sulfonate groups onto the lignosulfonate backbone.

Comparatively, individual lignin fragments extracted from soda pulping are not soluble in water, but their complexes with carbohydrates (hemicelluloses or hydrolysed cellulose) render them soluble in water (**12**), and consequently, favors the contribution of lignin fragments for mineral and soil aggregation (because the lignin-carbohydrate complex acts as surfactant).

The presence of lignin-carbohydrate complexes in soda and kraft liquor was also studied in the literature. Their water solubility and affinity to bind minerals were consistently reported. (**24,25,26,27**)**.**

Other relevant references from literature:

In fact, it is reported that lignin and lignin-carbohydrate complexes (LCCs) are less degraded after soda treatment than kraft treatment (**12**). In soda lignin, lignin-carbohydrate complexes consist of up to 34% of carbohydrates (meaning they are closer to their natural state) (**4**).

Concerning the application of soda lignin as binder, the literature clearly indicates that the soda lignin can be used as a low-cost and environmental binder, replacing the PVDF polymer in electrodes for rechargeable lithium batteries (**28**).

Hardwood soda lignin does not belong to a specific cluster but is a promising component of a plywood adhesive together with medium molar mass fractions of Sarkanda grass soda lignin (**4**).

Different works were performed in the literature to use the soda lignin as a binder in different applications. For example, sulfur-free lignins isolated from the soda pulping process were applied as plasticizers in the cement industry (**8, 29**). Black liquors from a soda pulping mill were also directly used in mortar to increase final concrete strength and to prevent corrosion in armed concrete (**30**).

The feasibility of using sulfur-free lignin (like soda lignin or native lignin) for soil stabilization was explored by some researchers (**31**).

Gopalakrishnan, K., Ceylan, H., and Kim, S. (2012) showed that soil that was stabilized by sulfur-free lignin may provide improved moisture retention (**32**).

Khalil

Khalil Jradi, PhD
Chemist,

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V. ANNEX

List of abbreviations:

NOSB: National Organic Standards Board (NOSB
OMRI: Organic Materials Review Institute

APPENDIX D:

MSDS’S sodium carbonate lignin

SAFETY DATA SHEET

SECTION 1 - PRODUCT IDENTIFICATION

Product Name & Synonyms: **Polybond**
Chemical Name: Sodium Carbonate Lignin

Manufacturer : Cascades Containerboard Packaging - Trenton
CAS #: 8068-05-1

Supplier's Name/Address: **Legnochem**
106 Lachance Drive
Sturgeon Falls, ON P2B 0B3
Tel: (705) 753-5709
Recommended Use: none
Restrictions on Use: none

SECTION 2 - HAZARDOUS IDENTIFICATION

Main Hazard: None
Flammability: Non-flammable
Chemical Hazard: None

Component:	% (Wt or Vol)	ACGIH TWA Units	ACGIH STEL Units	OSHA PEL Units
None	---	---	---	---

SECTION 3 - COMPOSITION / INFORMATION ON INGREDIENTS

Product Description : Sodium Lignin

SECTION 4 - FIRST AID MEASURE

Effects from Routine Use: None known
Effects of Overexposure : None known
Probable Routes of Exposure: Skin, eyes
Emergency & First Aid Procedures:

Eye Contact: Rinse immediately with water. Remove contact lenses; flush eyes with water. Consult a physician if necessary.
Skin Contact: Wash skin with soap and water.
Inhalation: Not applicable
Ingestion: Rinse mouth. Immediately dilute by drinking large quantities of water. After dilution, induce vomiting. Seek immediate medical attention. Never give anything by mouth to an unconscious person.

SECTION 5 - FIRE AND EXPLOSION DATA

Flash Point: Not applicable
Fire Extinguishing Media: Water and CO2
Flammable Limits (% by Vol): Lower Upper
Not Applicable
Special Firefighting Procedures & Equipment: Normal
Unusual Fire/Explosion Hazards: None

SECTION 6 - SPILL, LEAK, AND DISPOSAL PROCEDURES

Steps to be Taken in Case Material is Released or Spilled:

Liquids: Dam area to prevent spill from spreading This minimizes adverse effects on the environment Recover as much as possible of pure product in appropriate containers. Later, determine if this recovered product can be used for its intended purpose.

Wash area with water. Spills or releases of this material do not currently trigger the emergency release reporting requirements under the Federal Superfund Amendments and Reauthorization Act of 1986 (SARA). State and local laws may differ from federal law.

Waste Disposal Methods: Customary plant procedures for industrial waste treatment.

Environmental Precaution:

Do not discharge concentrated, undiluted product into streams, ponds, estuaries, oceans and other waters.

Resource Conservation & Recovery Action (RCRA) Requirements:

None known

Consult counsel for further guidance on local laws.

SECTION 7 - HANDLING AND STORAGE

Personal Protective Equipment:

Protective Gloves:	Rubber gloves recommended
Eye Protection:	Goggles recommended
Respiratory Protection (Specify Type):	Air-purifying respirator recommended for prolonged exposure to high concentrations.
Other Protective Equipment:	As appropriate to prevent bodily contact
Ventilation:	Recommended
Local Exhaust:	Recommended
Mechanical (General):	Recommended
Special:	None
Other:	None

SECTION 8 - EXPOSURE CONTROLS/PERSONAL PROTECTION

Personal Protection - respiratory:	Respiratory protection recommended.
Personal Protection - hand:	Product is not a skin irritant. Robber gloves are recommended.
Personal Protection - eye:	Safety glasses are required.
Personal Protection - skin:	Product is not a skin irritant.
Other Protection:	Eye wash fountain in the workplace is strongly recommended. Ensure adequate ventilation.

SECTION 9 - PHYSICAL AND CHEMICAL PROPERTIES

Physical State:	Viscous liquid.
Appearance & Odor:	Dark Brown liquid with wood odor
Boiling Point (oF):	100 C
Molecular Weight:	Unknown
Freezing Point (oF):	-8 C
Vapor Pressure (mm Hg):	Aqueous solution, like that of water
PH:	Approx. 7.0 – 9.0
Solubility in Water:	Completely Soluble

SECTION 10 - REACTIVITY DATA

Stability: Unstable__________Stable_______X_____

Conditions to Avoid: None known

Incompatibility (Materials to Avoid):

Caution needed with strong oxidizing agents

SECTION 11 - TOXICITY DATA

Local Effects:	None
Skin irritant :	None - this product is not classified as a skin irritant.
Eye Irritant:	None - this product is not classified as a skin irritant.

SECTION 12 - ECOLOGICAL INFORMATION

Ecological Information: none

SECTION 13 - DISPOSAL CONSIDERATIONS

Disposal Considerations: Dispose with accordance to local/national regulations governing the disposal of waste material.

SECTION 14 - TRANSPORT INFORMATION

Transport Information: None Known

SECTION 15 - REGULATORY INFORMATION

Regulatory Information: none-regulated

Summary: Not Toxic or harmful

SECTION 16 - OTHER INFORMATION

NON HAZARDOUS _ NON TOXIC

Other Precautions:	None known
Registrations/Certifications:	None
Effective Date:	January 2, 2018
Supersedes:	All previous editions

IMPORTANT:

The information above is believed to be accurate and represents the best information currently available to us. However, we make no warranty of merchantability or any other warranty, express or implied, with respect to such information, and we assume no liability resulting from its use. Users should make their own investigations to determine the suitability of the information for their particular purposes. In no event shall Legnochem be liable for any claims, losses, or damages of any third party or for lost profits or any special, indirect, incidental, consequential or exemplary damages, howsoever arising, even if Legnochem has been advised of the possibility of such damages.

Black Liquor

Safety Data Sheet

according to the federal final rule of hazard communication revised on 2012 (HazCom 2012)

Date of issue: 07/03/2015 Version: 1.0

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1. Product identifier

Product form	:	Mixture
Trade name	:	Black Liquor
Other means of identification	:	Spent liquor from soda pulping of wood

1.2. Relevant identified uses of the substance or mixture and uses advised against

Use of the substance/mixture	:	Additive

1.3. Details of the supplier of the safety data sheet

Sonoco Products Company
North Second Street
Hartsville, SC
USA 29550
Phone: 843-383-7000

1.4. Emergency telephone number

Emergency number	:	843-383-7000

SECTION 2: Hazards identification

2.1. Classification of the substance or mixture

GHS-US classification

Not classified

2.2. Label elements

GHS-US labeling

No labeling applicable

2.3. Other hazards

other hazards which do not result in classification	:	May cause slight irritation to eyes. May cause slight irritation to the skin.

2.4. Unknown acute toxicity (GHS-US)

Not applicable

SECTION 3: Composition/information on ingredients

3.1. Substance

Not applicable

3.2. Mixture

Name	Product identifier	%	GHS-US classification
Disodium carbonate	(CAS No) 497-19-8	0 - 2	Eye Irrit. 2A, H319

Full text of H-statements: see section 16

SECTION 4: First aid measures

4.1. Description of first aid measures

First-aid measures general	:	Never give anything by mouth to an unconscious person. If you feel unwell, seek medical advice (show the label where possible).
First-aid measures after inhalation	:	Allow breathing of fresh air. Allow the victim to rest.
First-aid measures after skin contact	:	Remove affected clothing and wash all exposed skin area with mild soap and water, followed by warm water rinse. Seek medical attention if irritation develops.
First-aid measures after eye contact	:	Rinse immediately with plenty of water. Obtain medical attention if pain, blinking or redness persist.
First-aid measures after ingestion	:	Rinse mouth. Do NOT induce vomiting. Obtain emergency medical attention.

4.2. Most important symptoms and effects, both acute and delayed

Symptoms/injuries	:	Not expected to present a significant hazard under anticipated conditions of normal use.
Symptoms/injuries after skin contact	:	Repeated or prolonged skin contact may cause irritation.
Symptoms/injuries after eye contact	:	May cause slight temporary irritation.

4.3. Indication of any immediate medical attention and special treatment needed

Treat symptomatically.

SECTION 5: Firefighting measures

5.1. Extinguishing media

Suitable extinguishing media : Foam. Dry powder. Carbon dioxide. Water spray. Sand.
Unsuitable extinguishing media : Do not use a heavy water stream.

5.2. Special hazards arising from the substance or mixture

Fire hazard : Incomplete combustion releases dangerous carbon monoxide, carbon dioxide and other toxic gases.
Explosion hazard : No direct explosion hazard.
Reactivity : Stable under normal conditions of use.

5.3. Advice for firefighters

Firefighting instructions : Use water spray or fog for cooling exposed containers. Exercise caution when fighting any chemical fire. Prevent fire-fighting water from entering environment.
Protective equipment for firefighters : Do not enter fire area without proper protective equipment, including respiratory protection.

SECTION 6: Accidental release measures

6.1. Personal precautions, protective equipment and emergency procedures

General measures : Spilled material may present a slipping hazard.

6.1.1. For non-emergency personnel

Protective equipment : Use personal protective equipment as required. For further information refer to section 8: "Exposure controls/personal protection".
Emergency procedures : Evacuate unnecessary personnel.

6.1.2. For emergency responders

Protective equipment : Equip cleanup crew with proper protection. For further information refer to section 8 : Exposure-controls/personal protection.
Emergency procedures : Ventilate area.

6.2. Environmental precautions

Prevent entry to sewers and public waters. Notify authorities if liquid enters sewers or public waters.

6.3. Methods and material for containment and cleaning up

For containment : Small spills: Flush residue with large amounts of water. Large spills: Clean up any spills as soon as possible, using an absorbent material to collect it.
Methods for cleaning up : Soak up spills with inert solids, such as clay or diatomaceous earth as soon as possible. Do not neutralize with acid. Collect spillage. Store away from other materials.

6.4. Reference to other sections

For further information refer to section 8 : Exposure-controls/personal protection. For disposal of residues refer to section 13 : Disposal considerations".

SECTION 7: Handling and storage

7.1. Precautions for safe handling

Precautions for safe handling : Wash hands and other exposed areas with mild soap and water before eating, drinking or smoking and when leaving work. Provide good ventilation in process area to prevent formation of vapor.
Hygiene measures : Handle in accordance with good industrial hygiene and safety practices. Wash hands and other exposed areas with mild soap and water before eating, drinking or smoking and when leaving work.

7.2. Conditions for safe storage, including any incompatibilities

Storage conditions : Store in open containers and/or vented containers. May be stored short-term in closed containers, but long-term storage in unvented containers should be avoided.
Incompatible materials : Strong acids. Strong oxidizers.

7.3. Specific end use(s)

No additional information available

SECTION 8: Exposure controls/personal protection

8.1. Control parameters

No additional information available

8.2. Exposure controls

Appropriate engineering controls : Either local exhaust or general room ventilation is usually required.
Personal protective equipment : Avoid all unnecessary exposure.

Materials for protective clothing	:	According to the conditions of use, protective gloves, apron, boots, head and face protection must be worn.
Hand protection	:	Wear protective gloves.
Eye protection	:	Chemical goggles or safety glasses.
Respiratory protection	:	No special respiratory protection equipment is recommended under normal conditions of use with adequate ventilation.
Other information	:	Do not eat, drink or smoke during use.

SECTION 9: Physical and chemical properties

9.1. Information on basic physical and chemical properties

Physical state	:	Liquid
Appearance	:	Liquid. Semi-solid.
Color	:	dark brown
Odor	:	Woody cooked sugar like
Odor threshold	:	No data available
pH	:	6 - 8
Melting point	:	No data available
Freezing point	:	No data available
Boiling point	:	≈ 212 °F
Flash point	:	> 212 °F
Relative evaporation rate (butyl acetate=1)	:	No data available
Flammability (solid, gas)	:	No data available
Explosive limits	:	No data available
Explosive properties	:	No data available
Oxidizing properties	:	No data available
Vapor pressure	:	same as water
Relative density	:	No data available
Relative vapor density at 20 °C	:	Not available
Density	:	≈ 0,85
Solubility	:	Water: Soluble
Log Pow	:	No data available
Log Kow	:	No data available
Auto-ignition temperature	:	No data available
Decomposition temperature	:	No data available
Viscosity	:	No data available
Viscosity, kinematic	:	No data available
Viscosity, dynamic	:	No data available

9.2. Other information

Percent Solids	:	35 – 40%

SECTION 10: Stability and reactivity

10.1. Reactivity

Stable under normal conditions of use.

10.2. Chemical stability

Hazardous polymerization will not occur.

10.3. Possibility of hazardous reactions

None known.

10.4. Conditions to avoid

Long-term storage in closed containers.

10.5. Incompatible materials

Strong acids. Strong oxidizers.

10.6. Hazardous decomposition products

On burning: release of carbon monoxide - carbon dioxide.

SECTION 11: Toxicological information

11.1. Information on toxicological effects

Likely routes of exposure	: Ingestion; Inhalation; Skin and eye contact
Acute toxicity	: Not classified (Based on available data, the classification criteria are not met)
Skin corrosion/irritation	: Not classified (Based on available data, the classification criteria are not met) pH: 6 - 8
Serious eye damage/irritation	: Not classified (Based on available data, the classification criteria are not met) pH: 6 - 8
Respiratory or skin sensitization	: Not classified (Based on available data, the classification criteria are not met)
Germ cell mutagenicity	: Not classified (Based on available data, the classification criteria are not met)
Carcinogenicity	: Not classified (Based on available data, the classification criteria are not met)
Reproductive toxicity	: Not classified (Based on available data, the classification criteria are not met)
Specific target organ toxicity (single exposure)	: Not classified (Based on available data, the classification criteria are not met)
Specific target organ toxicity (repeated exposure)	: Not classified (Based on available data, the classification criteria are not met)
Aspiration hazard	: Not classified (Based on available data, the classification criteria are not met)
Potential Adverse human health effects and symptoms	: Not expected to present a significant hazard under anticipated conditions of normal use.
Symptoms/injuries after skin contact	: Repeated or prolonged skin contact may cause irritation.
Symptoms/injuries after eye contact	: May cause slight temporary irritation.

SECTION 12: Ecological information

12.1. Toxicity

Ecology - general : Mixture not tested.

12.2. Persistence and degradability

Black Liquor	
Persistence and degradability	Not established.
Biochemical oxygen demand (BOD)	≈ 200 g O2/l 5d BOD

12.3. Bioaccumulative potential

Black Liquor	
Bioaccumulative potential	Not established.

12.4. Mobility in soil

No additional information available

12.5. Other adverse effects

Effect on ozone layer	: No additional information available
Effect on the global warming	: No additional information available
Other information	: Avoid release to the environment.

SECTION 13: Disposal considerations

13.1. Waste treatment methods

Waste disposal recommendations	: Dispose in a safe manner in accordance with local/national regulations.
Ecology - waste materials	: Avoid release to the environment.

SECTION 14: Transport information

Department of Transportation (DOT)

In accordance with DOT

Not regulated for transport

Additional information

Other information	:	No supplementary information available.

ADR

No additional information available

Transport by sea

No additional information available

Air transport

No additional information available

SECTION 15: Regulatory information

15.1. US Federal regulations

No additional information available

15.2. International regulations

CANADA

No additional information available

EU-Regulations

No additional information available

National regulations

No additional information available

15.3. US State regulations

No additional information available

SECTION 16: Other information

Other information	:	None.

Full text of H-statements:

Eye Irrit. 2A	Serious eye damage/eye irritation, Category 2A
H319	Causes serious eye irritation

SDS US (GHS HazCom 2012)

This information is based on our current knowledge and is intended to describe the product for the purposes of health, safety and environmental requirements only. It should not therefore be construed as guaranteeing any specific property of the product

BAKER
LIME

Material Safety Data Sheet

Printing date 10/20/2015 Reviewed on 10/20/2015

1 Identification

· **Product identifier**

· **Trade name: Pelletized Lime**

· **Other Names:** Baker's Premier Pellets
· **Relevant identified uses of the substance or mixture and uses advised against**
No further relevant information available.
· **Manufacturer/Supplier:**
Baker Lime
320 North Baker Road
York, PA 17408
· **Information department:** Compliance Department: 717-793-5463
· **Emergency telephone number:**
Chemtrec: 800-424-9300
Magnesita: 717-793-5463

2 Hazard(s) identification

· **Classification of the substance or mixture**

GHS08 Health hazard

Carc. 1A H350 May cause cancer.

· **Label elements**
· **GHS label elements**
The product is classified and labeled according to the Globally Harmonized System (GHS).
· **Hazard pictograms** GHS08
· **Signal word** Danger
· **Hazard statements**
H350 May cause cancer.
· **Precautionary statements**

P280	Wear protective gloves/protective clothing/eye protection/face protection.
P201	Obtain special instructions before use.
P202	Do not handle until all safety precautions have been read and understood.
P308+P313	IF exposed or concerned: Get medical advice/attention.
P405	Store locked up.
P501	Dispose of contents/container in accordance with local/regional/national/international regulations.

· **Carcinogenicity:**
The International Agency for Research on Cancer (IARC) has classified crystalline silica as a Group 1 Carcinogen "sufficient evidence of carcinogenicity in humans".
· **Other hazards**
· **Results of PBT and vPvB assessment**
· **PBT:** Not applicable.
· **vPvB:** Not applicable.

(Contd. on page 2)

Material Safety Data Sheet

(Contd. of page 1)

3 Composition/information on ingredients

· **Chemical characterization: Substances**

· **CAS No. Description**		
16389-88-1	dolomite	50-100%
	Sodium Salt Lignin Binder	<5%
14808-60-7	Crystalline Silica, Quartz	<1%

· **Chemical characterization: Mixtures**
· **Description:**
Mixture: consisting of the following components.
Refer to product data sheet for more details.

4 First-aid measures

· **Description of first aid measures**
· **After inhalation:**
Supply fresh air; consult doctor in case of complaints.
Seek medical treatment in case of complaints.
· **After skin contact:**
Wash with water and soap
Immediately rinse with water.
· **After eye contact:** Rinse opened eye for several minutes under running water.
· **Information for doctor:**
· **Most important symptoms and effects, both acute and delayed**
No further relevant information available.
· **Indication of any immediate medical attention and special treatment needed**
No further relevant information available.

5 Fire-fighting measures

· **Extinguishing media**
· **Suitable extinguishing agents:**
CO2, extinguishing powder or water spray. Fight larger fires with water spray or alcohol resistant foam.
· **Special hazards arising from the substance or mixture** No further relevant information available.
· **Advice for firefighters**
· **Protective equipment:** No special measures required.

6 Accidental release measures

· **Personal precautions, protective equipment and emergency procedures** Not required.
· **Environmental precautions:**
Do not allow product to reach sewage system or any water course.
Inform respective authorities in case of seepage into water course or sewage system.
Do not allow to enter sewers/ surface or ground water.
· **Methods and material for containment and cleaning up:**
Dispose contaminated material as waste according to item 13.
Ensure adequate ventilation.

(Contd. on page 3)

Material Safety Data Sheet

(Contd. of page 2)

· **Reference to other sections**
See Section 7 for information on safe handling.
See Section 8 for information on personal protection equipment.
See Section 13 for disposal information.

7 Handling and storage

· **Handling:**
· **Precautions for safe handling**
Ensure good ventilation/exhaustion at the workplace.
Open and handle receptacle with care.
· **Information about protection against explosions and fires:**
Keep respiratory protective device available.

· **Conditions for safe storage, including any incompatibilities**
· **Storage:**
· **Requirements to be met by storerooms and receptacles:** No special requirements.
· **Information about storage in one common storage facility:** Not required.
· **Further information about storage conditions:**
Keep receptacle tightly sealed.
Store in dry conditions.
Store in a cool place.
· **Specific end use(s)** No further relevant information available.

8 Exposure controls/personal protection

· **Additional information about design of technical systems:** No further data; see item 7.

· **Control parameters**

· **Components with limit values that require monitoring at the workplace:**	
14808-60-7 Crystalline Silica, Quartz (<1%)	
PEL (USA)	see Quartz listing
REL (USA)	Long-term value: 0.05* mg/m³ *respirable dust; See Pocket Guide App. A
TLV (USA)	Long-term value: 0.025* mg/m³ *as respirable fraction
EL (Canada)	Long-term value: 0.025 mg/m³ ACGIH A2; IARC 1
EV (Canada)	Long-term value: 0.10* mg/m³ *respirable fraction

· **Additional information:** The lists that were valid during the creation were used as basis.

· **Exposure controls**
· **Personal protective equipment:**
· **General protective and hygienic measures:**
Keep away from foodstuffs, beverages and feed.
Immediately remove all soiled and contaminated clothing.
Wash hands before breaks and at the end of work.
Store protective clothing separately.

(Contd. on page 4)

(Contd. of page 3)

· **Breathing equipment:**
In case of brief exposure or low pollution use respiratory filter device. In case of intensive or longer exposure use respiratory protective device that is independent of circulating air.
Suitable respiratory protective device recommended.

· **Protection of hands:**

Protective gloves

· **Material of gloves**
The selection of the suitable gloves does not only depend on the material, but also on further marks of quality and varies from manufacturer to manufacturer. As the product is a preparation of several substances, the resistance of the glove material can not be calculated in advance and has therefore to be checked prior to the application.

9 Physical and chemical properties

· **Information on basic physical and chemical properties**	
· **General Information**	
· **Appearance:**	
Form:	Solid
Color:	Light brown
· **Odor:**	Characteristic
· **Odour threshold:**	Not determined.
· **pH-value:**	Not applicable.
· **Change in condition**	
Melting point/Melting range:	Undetermined.
Boiling point/Boiling range:	Undetermined.
· **Flash point:**	Not applicable.
· **Flammability (solid, gaseous):**	Not determined.
· **Decomposition temperature:**	Not determined.
· **Auto igniting:**	Product is not selfigniting.
· **Danger of explosion:**	Product does not present an explosion hazard.
· **Explosion limits:**	
Lower:	Not determined.
Upper:	Not determined.
· **Vapor pressure:**	Not applicable.
· **Density:**	Not determined.
· **Relative density**	Not determined.
· **Vapour density**	Not applicable.
· **Evaporation rate**	Not applicable.
· **Solubility in / Miscibility with**	
Water:	Slightly soluble.

(Contd. on page 5)

(Contd. of page 4)

· **Partition coefficient (n-octanol/water):** Not determined.

· **Viscosity:**
Dynamic: Not applicable.
Kinematic: Not applicable.
· **Other information** No further relevant information available.

10 Stability and reactivity

· **Possibility of hazardous reactions** No dangerous reactions known.
· **Conditions to avoid** No further relevant information available.
· **Incompatible materials:** No further relevant information available.
· **Hazardous decomposition products:** No dangerous decomposition products known.
· **Additional information:** None

11 Toxicological information

· **Information on toxicological effects**
· **Primary irritant effect:**
· **on the skin:** No irritant effect.
· **on the eye:** No irritating effect.
· **Sensitization:** No sensitizing effects known.

· **Carcinogenic categories**

· **IARC (International Agency for Research on Cancer)**			
14808-60-7	Crystalline Silica, Quartz	1	<1%

· **NTP (National Toxicology Program)**			
14808-60-7	Crystalline Silica, Quartz	K	<1%

· **OSHA (Occupational Safety & Health Administration)**
None of the ingredients is listed.

12 Ecological information

· **Toxicity**
· **Aquatic toxicity:** No further relevant information available.
· **Persistence and degradability** No further relevant information available.
· **Behavior in environmental systems:**
· **Bioaccumulative potential** No further relevant information available.
· **Mobility in soil** No further relevant information available.
· **Additional ecological information:**
· **General notes:**
Do not allow undiluted product or large quantities of it to reach ground water, water course or sewage system.
Water hazard class 1 (Self-assessment): slightly hazardous for water
· **Results of PBT and vPvB assessment**
· **PBT:** Not applicable.
· **vPvB:** Not applicable.

(Contd. on page 6)

(Contd. of page 5)

· **Other adverse effects** No further relevant information available.

13 Disposal considerations

· **Uncleaned packagings:**
· **Recommendation:** Disposal must be made according to official regulations.

14 Transport information

· **Class**	Void
· **Environmental hazards:**	Not applicable.
· **Special precautions for user**	Not applicable.
· **Transport in bulk according to Annex II of MARPOL73/78 and the IBC Code**	Not applicable.
· **Remarks:**	Not Applicable This product is not a hazardous material as defined in 49 U.S. CFR Part 172. It is not defined as hazardous in the IATA Regulations, Section 4.2.
· **UN "Model Regulation":**	-

15 Regulatory information

· **Safety, health and environmental regulations/legislation specific for the substance or mixture**

· **Section 313 (Specific toxic chemical listings):**

None of the ingredients is listed.

· **TSCA (Toxic Substances Control Act):**
All ingredients are listed.

16389-88-1	dolomite
14808-60-7	Crystalline Silica, Quartz

· **Chemicals known to cause cancer:**

14808-60-7	Crystalline Silica, Quartz	<1%

· **Chemicals known to cause reproductive toxicity for females:**

None of the ingredients is listed.

· **Chemicals known to cause reproductive toxicity for males:**

None of the ingredients is listed.

· **Chemicals known to cause developmental toxicity:**

None of the ingredients is listed.

· **GHS label elements**
The product is classified and labeled according to the Globally Harmonized System (GHS).
· **Hazard pictograms** GHS08
· **Signal word** Danger

(Contd. on page 7)

(Contd. of page 6)

· **Hazard statements**
H350 May cause cancer.

· **Precautionary statements**

P280	Wear protective gloves/protective clothing/eye protection/face protection.
P201	Obtain special instructions before use.
P202	Do not handle until all safety precautions have been read and understood.
P308+P313	IF exposed or concerned: Get medical advice/attention.
P405	Store locked up.
P501	Dispose of contents/container in accordance with local/regional/national/international regulations.

· **Chemical safety assessment:** A Chemical Safety Assessment has not been carried out.

16 Other information

This information is based on our present knowledge. However, this shall not constitute a guarantee for any specific product features and shall not establish a legally valid contractual relationship.

· **Recommended restriction of use** For professional use only

· **Date of preparation / last revision** 10/20/2015 / 7

· **Abbreviations and acronyms:**
Carc. 1A: Carcinogenicity, Hazard Category 1A

Oldcastle®
Industrial Minerals

MATERIAL SAFETY DATA SHEET (MSDS) FOR PELLETIZED LIMESTONE

(Complies with OSHA's Hazard Communication Standard, 29 CFR 1910.1200)

Section 1 - IDENTIFICATION

Supplier/Manufacturer	Emergency Contact Information
Oldcastle® Stone Products 550 S. Biesecker Road Thomasville, PA 17364	(717) 792-2631 (Laboratory - Ext. 235)

Product name and synonyms

Limestone Pellets, Pelletized Limestone, Pelletized
Lime, Pellet Lime, Calcitic Pellets, YardRight, Clean Lime

Chemical family	Formula
Limestone/Dolomite (CAS #1317-65-3)	$CaCO_3$ – (52.0-87.0%) $MgCO_3$ – (12.0-40.0%)
Sodium Carbonate Lignin (CAS#8061-51-6) Ammonium Lignin Sulfonate (CAS#8061-53-8) Sodium Lignin Sulfonate (CAS#8061-51-6)	(3-5%) See accompanying Material Safety Data Sheet

Section 2 - COMPONENTS

Hazardous Ingredients

Respirable quartz (CAS# 14808-60-7) – greater than 0.1% by weight
ACGIH TLV-TWA (1997) = 0.10 mg respirable quartz dust/m^3
OSHA PEL (8-hour TWA) = (10 mg respirable dust/$m^{3)}$/(percent silica + 2)
NIOSH REL (8-hour TWA) = 0.05 mg respirable dust/m^3

Section 3 - HAZARD IDENTIFICATION

Potential Health Effects

Relevant Routes of Exposure:
Eye contact, skin contact, inhalation, and ingestion.

Effects Resulting from Eye Contact:
Exposure to airborne dust may cause immediate or delayed irritation or inflammation. Eye contact by large amounts of dry powder or splashes of wet limestone dust may cause effects ranging from moderate eye irritation to chemical burns or blindness. Such exposures may require immediate first aid (see Section 4) and medical attention to prevent damage to the eye.

Effects Resulting from Skin Contact:
Direct contact may cause irritation by mechanical abrasion.

Effects Resulting from Inhalation:
Limestone may contain trace amounts of free crystalline silica. Prolonged exposure to respirable free silica can aggravate other lung conditions and cause silicosis, a disabling and potentially fatal lung disease.

Exposure to limestone dust may cause irritation to the moist mucous membranes of the nose, throat, and upper respiratory system. It may also leave unpleasant deposits in the nose.

Effects Resulting from Ingestion:
Although small quantities of dust are not known to be harmful, ill effects are possible if larger quantities are consumed.

Carcinogenic potential:
Limestone is **not** listed as a carcinogen by NTP, OSHA, or IARC. It may however, contain trace amounts of substances listed as carcinogens by these organizations.

Crystalline silica, which is a component of limestone, is now classified by IARC as known human carcinogen (Group I). NTP has characterized respirable silica as "reasonably anticipated to be [a] carcinogen".

Medical conditions which may be aggravated be, inhalation or dermal exposure:
Pre-existing upper respiratory and lung diseases.

Section 4 - FIRST AID

Eyes
Immediately flush eyes thoroughly with water. Continue flushing eye for at least 15 minutes, including under lids, to remove all particles. Call physician if irritation persists or later develops.

Skin
Wash skin with cool water and pH-neutral soap or a mild detergent. Seek medical treatment if irritation persists or later develops.

Inhalation of Airborne Dust
Remove to fresh air. Seek medical help if coughing and other symptoms do not subside.

Ingestion
Do not induce vomiting. If conscious, have the victim drink plenty of water and call a physician immediately.

Section 5 - FIRE AND EXPLOSION DATA

Flash point ....None
Upper Explosive Limit.................None
Extinguishing media.....................Not Combustible
Hazardous combustion products..None

Lower Explosive Limit................…....None
Auto ignition temperature..............….Not Combustible
Special fire fighting Procedures....….....None
Unusual fire and explosion hazards…..None

Section 6 - ACCIDENTAL RELEASE MEASURES

Collect dry material using a scoop. Avoid actions that cause dust to become airborne. Avoid inhalation of dust and contact with skin.

None of the components of this product are subject to the reporting requirements of Title III of SARA 1986, and 40 CFR 372.

Section 7 - HANDLING AND STORAGE

Follow the personal protection and controls set forth in Section 8 of this MSDS when handling this product. Respirable crystalline silica-containing dust may be generated during processing, handling and storage.

Section 8 - EXPOSURE CONTROLS/PERSONAL PROTECTION

Skin Protection
Wash dust-exposed skin with soap and water before eating, drinking, smoking, and using the toilet facilities. Wash work cloths after each use.

Respiratory Protection
Avoid actions that cause dust to become airborne. Use local or general exhaust ventilation to control exposures below applicable exposure limits.

Use NIOSH/MSHA approved (under 30 CFR 11) or NIOSH approved (under 42 CFR 84) respirators in poorly ventilated areas, if an applicable exposure limit is exceeded, or when dust causes discomfort or irritation. (Advisory: Respirators and filters purchased after June 10, 1998 must be certified under 42 CFR 84.)

Ventilation
Use local exhaust or general dilution ventilation to control exposure within applicable limits.

Eye Protection
Safety glasses with side shields should be worn as minimum protection. In extremely dusty environments and unpredictable environments wear unvented or indirectly vented goggles to avoid eye irritation or injury. Contact lenses should not be worn when

working with products which may generate airborne dust.

Section 9 - PHYSICAL AND CHEMICAL, PROPERTIES

Physical state...........Pourous
Solubility in water...Limestone - Negligible
Binder (Lignin) – High
Vapor density..........Not applicable
Melting point...........Not applicable

Odor................……………......Binder may have a slight scent (lignin)
Vapor pressure..........…….…...Not applicable
Evaporation rate..……………...Not applicable
Boiling point......……………......Not applicable (i.e., > 1000 C)
Specific gravity (H20 = 1.0)…....2.55-2.85

Section 10 - STABILITY AND REACTIVITY

Stability

Stable.

Conditions to avoid

Avoid contact with incompatible materials (see below).

Incompatibility

Materials to avoid include; powerful oxidizing agents such as flouride, boron triflouride, chlorine triflouride, manganese triflouride, and oxygen deflouide. Contact of these materials may cause fire and/or explosions. Silica disolves n hydroflouric acid producing a corrosive gas – silicon tetraflouride.

Hazardous decomposition

Will not spontaneously occur. Silica-containing respirable dust particles may be generated by handling.

Hazardous Polymerization

Will not occur.

Section 11 - TOXICOLOGICAL INFORMATION

For a description of available, more detailed toxicological information contact the supplier or manufacturer.

Section 12 - ECOLOGICAL INFORMATION

Ecotoxicity

No recognized unusual toxicity to plants or animals

Relevant physical and chemical properties

(See Sections 9 and 10.)

Section 13 - DISPOSAL

Pickup and reuse clean materials. Dispose of waste materials in accordance with applicable federal, state, and local laws and regulations.

Where applicable, dispose of bags in an approved landfill or incinerator.

Section 14 - TRANSPORTATION DATA

Hazardous materials description/proper shipping name

Not hazardous under U.S. Department of Transportation (DOT) regulations.

Hazard class	Identification number
Not applicable.	Not applicable

Required label text	Hazardous substances/reportable quantities (RQ)
Not applicable.	Not applicable.

Section 15 - OTHER REGULATORY INFORMATION

Status under USDOL-OSHA Hazard Communication Rule, 29 CFR 1910.1200

Pelletized limestone is considered a "hazardous chemical" under this regulation, and should be part of any hazard communication program.

Status under CERCLA/SUPERFUND 40 CFR 117 and 302

Not listed.

Hazard Category under SARA(Title III), Sections 311 and 312

Pelletized limestone qualifies as a "hazardous substance" with delayed health effects.

Status under SARA (Title III), Section 313

Not subject to reporting requirements under Section 313.

Status under TSCA (as of May 1997)

Some substances in limestone are on the TSCA inventory list.

Status under the Federal Hazardous Substances Act

Pelletized limestone is a "hazardous substance" subject to statutes promulgated under the subject act.

Status under California Proposition 65

This product contains up to 0.05 percent of chemicals (trace elements) known to the State of California to cause cancer, birth defects or other reproductive harm. California law requires the manufacturer to give the above warning in the absence of definitive testing to prove that the defined risks do not exist.

Section 16 - OTHER INFORMATION

Prepared by

Lance Griffin
Plant Manager
Oldcastle® Stone Products
550 S. Biesecker Road
Thomasville,
PA. 17364
(717) 792 - 2631

Approval date or Revision date

Approved: February, 1999
Revised: October, 2002

Other important information

This product should only be used by knowledgeable persons. While the information provided in this material safety data sheet is believed to provide a useful summary of the hazards this product as it is commonly used, the sheet cannot anticipate and provide the all of the information that might be needed in every situation. Inexperienced product users should obtain proper training before using this product.

SELLER MAKES NO WARRANTY, EXPRESSED OR IMPLIED, CONCERNING THE PRODUCT OR THE MERCHANTABILITY OR FITNESS THEREOF FOR ANY PURPOSE OR CONCERNING THE ACCURACY OF ANY INFORMATION PROVIDED BY Oldcastle® Stone Products except that the product shall conform to contracted specifications. The information provided herein was believed by Oldcastle® Stone Products to be accurate at the time of preparation or prepared from sources believed to be reliable, but it is the responsibility of the user to investigate and understand other pertinent sources of information to comply with all laws and procedures applicable to the safe handling and use of product and to determine the suitability of the product for its intended use. Buyer's exclusive remedy shall be for damages and no claim of any kind, whether as to product delivered or for non-delivery of product, and whether based on contract, breach of warranty, negligence, or otherwise shall be greater in amount than the purchase price of the quantity of product in respect of which damages are claimed. In no event shall Seller be liable for incidental or consequential damages, whether Buyer's claim is based on contract, breach of warranty, negligence or otherwise.

Pro-Feed

PELLETING AGENT FOR LIVESTOCK FEED

Pro-Feed is an all purpose pellet binder

Directions

Use 5 kg per tonne of feed to be pelletized.

Store in a cool dry place.

Consult the Compendium of Medicating Ingredient Brochures for acceptable drug Compatibilities with this product

Registration Number: 990368

INGREDIENTS

Sodium Carbonate Lignin Dehydrated

CAUTION

Avoid contact with skin and eyes.
Avoid breathing dust.
Close bag after each use.

GUARANTEED ANALYSIS

Moisture(max.)	5 %
Ash(max.)	11 %

Northway Lignin Chemical

756 Coursol Road
Sturgeon Falls, ON P2B 3J5
705-753-2757

Net Weight

25 kg

APPENDIX E:

Example lab analyses of sodium carbonate lignin liquor

AGRI-FOOD LABORATORIES
AgTest®
Unit 1, 503 Imperial Road North, Guelph, Ontario N1H 6T9 (519) 837-1600

Analytical Report

Report# 240483

Page 1 of 1

Copy Sent To: Email

Norampac Inc - Patrick Lemaire, Cascades Canada Inc/MH
Charest
752 Rue Sherbrooke Ouest
Montreal , QC
H3A 1G1
Email: marie-helene_charest@cascades.com

Date Received: 28-Feb-2005

Date Printed: 02-Mar-2005

Laboratory Number: 6230402

Sample Number: 2

Sample Description: Fresh Black Liquor Evaporator

These results are reported on an 'as is' basis.

Moisture %	52.65
Protein % (N X 6.25)	1.04
Calcium %	0.33
Phosphorus %	0.01
Sodium %	5.96
Potassium %	0.36
Magnesium %	0.04
Zinc (ppm)	9.52
Manganese (ppm)	36.19
Copper (ppm)	6.12
Iron (ppm)	72.25
Neutral Detergent Fibre %	< 0.5
Lignin %	0.01
Dextrose(%)	8.21

These results pertain solely to the sample(s) received by the laboratory.
This report shall not be reproduced without the written consent of Agri-Food Laboratories.

Authorized by: *Papken Bedirian*
Director Technical Services

Method References:
Moist: AOAC 930.15, CP: AOAC 990.03, Ca%: AOAC 985.01, P%: AOAC 985.01, Na%: AOAC 985.01, K%: AOAC 985.01, Mg%: AOAC 985.01, Zn: AOAC 985.01, Mn: AOAC 985.01, Cu: AOAC 985.01, Fe: AOAC 985.01

Analysis Report

GM16-04882

Legnochem
106 Lachance Drive
Sturgeon Falls, ON P2B 0B3

Received : 08-Nov-2016
Completed : 14-Nov-2016
Order Reference : Denis Legnochem - Sonoco S Carolina Div.

Laboratory ID:	GM16-04882.001
Client Sample #:	8068-05-1
Description:	Polybond S
Moisture (%)	62.62
Sodium (%)	5.32
pH	9.34
Dextrose (%)	8.00

Applied methods:

Moisture: A201/A202

Minerals: A204a

NOTE:
The analysis report above refers to the time and place of testing, and strictly to the supplied sample(s) only, without reference to any other matter. This report does not evidence or refer to any consignment or shipment or/and SGS sampling and inspection.

Report File Reference Number: 0000036803

Signed and dated in Guelph, ON
On 14-Nov-2016

For and on behalf of SGS Canada Inc., Agriculture and Food

David Boyle

David Boyle, PhD
Senior Chemist