Identification of Petitioned Substance

<table>
<thead>
<tr>
<th>Chemical Names:</th>
<th>28</th>
<th>CAS Numbers:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin sulfonate</td>
<td>29</td>
<td>8062-15-5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Other Names:</th>
</tr>
</thead>
<tbody>
<tr>
<td>lignosulfonate</td>
</tr>
<tr>
<td>lignosulfuric acid</td>
</tr>
<tr>
<td>lignosulfonic acid</td>
</tr>
<tr>
<td>LST 7</td>
</tr>
<tr>
<td>Ligninsulonic acid</td>
</tr>
<tr>
<td>Poly(lignosulfonic acid)</td>
</tr>
<tr>
<td>Protectol W</td>
</tr>
<tr>
<td>Sulfite lignin</td>
</tr>
</tbody>
</table>

| (NLM, 2011a) |

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

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

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 cannories. 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

<table>
<thead>
<tr>
<th>Chemical or Physical Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Light tan to dark brown† ‡ (CAMEO, Undated-a; CAMEO, Undated-b)</td>
</tr>
<tr>
<td>Physical State</td>
<td>Solid (powder) (Hawley, 1981)</td>
</tr>
<tr>
<td>Odor</td>
<td>Odorless (CAMEO, Undated-a)</td>
</tr>
<tr>
<td>Melting Point</td>
<td>Decomposes at &gt;200°C (&gt;392°F) (Hawley, 1981)</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>Exists in a solid state</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in water† (FAO, 2008)</td>
</tr>
<tr>
<td>Reactivity</td>
<td>Lignin sulfonates are corrosive to aluminum and aluminum alloys in the absence of calcium carbonate (CPWA, 2005)</td>
</tr>
<tr>
<td>Oxidizing or Reduction Action</td>
<td>React as acids to neutralize bases. Usually do not react as reducing or oxidizing agents (CAMEO, Undated-a)‡</td>
</tr>
<tr>
<td>Flammability/Flame Extension</td>
<td>Flash point data not available although probably combustible (CAMEO, Undated-a)‡</td>
</tr>
<tr>
<td>Explodability</td>
<td>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)</td>
</tr>
</tbody>
</table>

*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)† (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 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, 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

† 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 1 percent (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.

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**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 cleaners? (B) Is the substance a synthetic inert ingredient that is not classified by the EPA as inert 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).
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 (CO₂). 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 CO₂. The CO₂ 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 LC₅₀ 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 pulp 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 (SO₂), 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).

**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)).**

**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.

**Use:** 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).

**Misuse:** 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 SO₂, 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.

**Disposal:** 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, sulfinic acid groups, and CO₂ are liberated (Selin et al., 1975). The breakdown of a large amount of lignin sulfonate in the soil (resulting in the release of additional CO₂) could acidify the soil (CO₂ 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).

**Evaluation Question #9:** 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.

**Evaluation Question #10:** 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 1 percent 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 “safering” 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).

**References:**


Washington State University – Tree Fruit Research and Extension Center. 7(2): 5-7.


