

Lignin Sulfonate

Crops

Identification of Petitioned Substance

1			
2			
3	Chemical Names:	28	CAS Numbers:
4	Lignin sulfonate	29	8062-15-5
5		30	Lignosulfonate salts:
6	Other Names:	31	8061-51-6 (sodium lignosulfonate)
7	lignosulfonate	32	8061-54-9 (magnesium lignosulfonate)
8	lignosulfuric acid	33	8061-53-8 (ammonium lignosulfonate)
9	lignosulfonic acid	34	8061-52-7 (calcium lignosulfonate)
10	LST 7	35	(U.S. EPA, 2010a)
11	Ligninsulonic acid		
12	Poly(lignosulfonic acid)		Other Codes:
13	Protectol W		705707 (USEPA PC Code [U.S. EPA 2010b])
14	Sulfite lignin		160226 (EPA Reference ID)
15	(NLM, 2011a)		705705, 705708-705714 (U.S. EPA PC Code [U.S.
16	There are also various salts of lignin sulfonate		EPA, 2010b], various lignosulfonate salts)
17	listed in the CAS Numbers section.		1522 (CODEX Alimentarius Commission INS
18			Number, calcium lignosulfonate)
19	Trade Names:		
20	Lignosite® - Georgia-Pacific (Georgia-Pacific		
21	West, Inc., 2000)		
22	BorrePlex - LignoTech USA, Inc. (OMRI, 2010)		
23	Phyto-Plus® Plant Stimulator - Baicor L.C.		
24	(OMRI, 2010)		
25	SHADOW - LignoTech USA, Inc. (OMRI, 2010)		
26	Orzan - ITT Rayonnier (Sugar and Spotts, 1986)		
27			

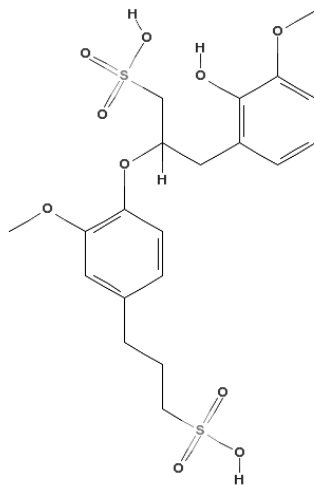
Characterization of Petitioned Substance

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.

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61
62 **Figure 1. Chemical Structure of Lignin Sulfonate (NLM, 2011b)**
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65 **Properties of the Substance:**

66
67 A molecular weight of 490.5 g/mol has been reported for lignin sulfonate (NLM, 2011b). Other reports on
68 the lignin sulfonates as a group state that they may have molecular weights ranging from 1,000 to 20,000
69 daltons, or higher (up to 100,000 daltons in some cases) depending on their composition (Zhor and
70 Bremner, 1999; Hawley, 1981). Weight-average molecular weights of calcium lignosulfonate are reported
71 to range from 40,000 to 65,000 (unitless). Calcium lignosulfonate is soluble in water and insoluble in
72 organic solvents (FAO, 2008).
73

74 Other physical and chemical properties of lignin sulfonate are presented in Table 1. The properties
75 presented in Table 1 describe lignin sulfonate generally, unless a specific salt is otherwise indicated.
76

77 **Specific Uses of the Substance:**

78
79 Lignin sulfonate may be used in organic crop production as a plant or soil amendment (dust suppressant,
80 chelating agent) and a floatation agent for postharvest handling of products (e.g., pears). Chelating agents
81 are large, organic molecules that are used to envelop highly-reactive trace metal ions. The purpose of
82 chelates is to incorporate metal ions into a soluble but bound form that is capable of supplying nutrients to
83 plants. As the chelate breaks down, the metal ion micronutrients are slowly released into the soil in a
84 bioavailable form that may be taken up by the plant (Jones and Jacobsen, 2009). Two manufacturers
85 produce products containing lignin sulfonate—LignoTech USA, Inc. and Baicor, L.C. (OMRI, 2010).
86 LignoTech manufactures five products and Baicor, L.C. manufactures one product (OMRI, 2010).
87

88 Lignin sulfonates have also been investigated for their potential as chelating agents for the complexation of
89 metal ions, including copper, magnesium, and mercury, for the purpose of environmental remediation.
90 Garcia-Valls et al. (2001) cited the biodegradability and relatively inexpensive nature of the lignin
91 sulfonates as factors supporting their use in remediation. Lignin sulfonates have also been used in
92 bioremediation at dairy operation facilities and meat and seafood canneries. Lignin sulfonates were
93 applied to waste streams at the facilities to help remove dairy and seafood waste. The lignin sulfonates
94 formed complexes with the waste materials, which then precipitated out of wash solutions. This process
95 allowed for diversion of some food waste from waterways. The resulting food waste/lignin sulfonate
96 complex was then used in animal feed (USDA, 1969).
97

98
99

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

100
101 Calcium lignosulfonate may be used as an inert ingredient or adjuvant (mixing agent/sticking aid) in
102 pesticide products, except for those exempt under Section 25(b) of the Federal Insecticide, Fungicide, and
103 Rodenticide Act (FIFRA)¹ (OMRI 2010; CFR, 2003a; CFR, 2003b; CFR, 2003c). Calcium lignosulfonate is
104 also used as an encapsulating agent or carrier for fat-soluble carotenoids, vitamins, and other functional
105 ingredients in foods such as vitamin drinks, fruit-based beverages, hard candies, and dairy products
106 (Toledo and Kuznesof, 2008). As discussed in the “Composition of the Substance” section, other lignin
107 sulfonate salts are included in the OMRI Generic Materials List (OMRI 2010), but little specific information
108 is available about them.

109
110 **Approved Legal Uses of the Substance:**
111

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

119
120 Calcium lignosulfonate (CAS No. 8061-52-7) and sodium lignosulfonate (CAS No. 8061-51-6) may be used
121 as inert ingredients in pesticide products. These inert ingredients are on EPA’s inert ingredients list (List
122 4B) which, in combination with List 4A, was used as a reference for allowed inert ingredients in organic
123 pesticide products. In 2006, EPA changed its classification system for inert ingredients, but lists 4A and 4B
124 are still maintained for their use by the NOP. The NOP still allows inert ingredients on these lists to be
125 used as inert ingredients in pesticide products unless the ingredients were removed following EPA

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

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

128
129 Ammonium lignosulfonate is allowed, with restrictions, for use as a nutrient chelate in organic fertilizer
130 products. Formulated fertilizer products that contain ammonium lignosulfonate may not make nitrogen
131 claims on the label and/or the contribution of ammonium lignosulfonate to the total nitrogen content of
132 the formulated product must be less than 1percent (OMRI 2010; CFR, 2003a; CFR, 2003b; CFR, 2003c).
133 Lignin sulfonate is exempt from the requirement of a tolerance when used as an inert ingredient in pre-
134 and post-harvest agricultural production and as an inert ingredient applied to animals (CFR, 2004a; CFR,
135 2004b). Tolerances are acceptable levels of pesticide residues on food products that are set by the U.S. EPA,
136 and enforced by the USDA and FDA. According to 40 CFR 180.900, "An exemption from a tolerance shall
137 be granted when it appears that the total quantity of the pesticide chemical in or on all raw agricultural
138 commodities for which it is useful under conditions of use currently prevailing or proposed will involve no
139 hazard to the public health."

141 Action of the Substance:

142
143 Lignin sulfonate acts as a dust suppressant by its large size and affinity for binding with other polar and
144 nonpolar compounds. The smaller dust compounds adsorb to the lignin sulfonate and form a larger,
145 heavier complex that is not as friable, which suppresses the dust (CWPA, 2005). Lignin sulfonate is used as
146 a micronutrient chelate because it is a large compound with multiple polar and nonpolar moieties. The
147 relatively smaller, charged micronutrient ions, such as boron, manganese, and iron, are bound to the large
148 lignin sulfonate molecule and are slowly released into the soil in a bioavailable form (Jones and Jacobsen,
149 2009). Lignin sulfonate will help stabilize emulsions by acting as a surfactant. Lignin sulfonate dissolved
150 in water is mixed with oil and preferentially adsorbs to the oil molecules, forming a barrier at the interface
151 between the oil and water, which stabilizes the emulsion (Gundersen and Sjoblom, 1999; LignoTech, 2009).
152 When used as a flotation aid, lignin sulfonate is added to the dump water to increase the density of the
153 water. This is necessary for fruits like pears that may be heavier than water. Increasing the density of the
154 water with lignin sulfonate allows the pears to float, and therefore the pears are less likely to be damaged
155 in processing (Agar and Mitcham, 2000).

157 Combinations of the Substance:

158
159 Through its use as an emulsifier and adjuvant, lignin sulfonates (calcium lignosulfonate and sodium
160 lignosulfonate) may be combined with various pesticide active ingredients that act as insecticides or
161 herbicides (NOSB, 2009; OMRI, 2010; CFR, 2003a; CFR, 2003b; CFR, 2003c).

163 Status

165 Historic Uses:

166
167 Lignin sulfonate has been used in organic agricultural production as a dust suppressant, chelating agent
168 for micro- and macronutrient fertilizer applications, flotation agent in pear production, and as an
169 emulsifier and stabilizer for pesticide applications. A previous technical report for lignin sulfonate was
170 created as part of the 1995 petition process to add lignin sulfonate to the National Organic Standards Board
171 (NOSB) National List (NOSB, 1995).

172
173 Lignin sulfonate has been investigated for its potential as a chelating agent in the environmental
174 remediation of heavy metals and in the remediation of food processing wastes (Garcia-Valls et al., 2001;
175 USDA, 1969). Lignin sulfonate also has been used as an encapsulating agent for vitamins and other
176 ingredients in food products (Toledo and Kuznesof, 2008).

177

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

184

185 **OFPA, USDA Final Rule:**

186

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

190

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

192

- 193 • 205.601(j)(4) - Lignin sulfonate - chelating agent, dust suppressant, floatation agent
- 194
- 195 • 205.601(l) - As floating agents in postharvest handling; (1) Lignin sulfonate

196

197 **International:**

198

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

202

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

208

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

215

216

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

217

218 **Evaluation Question #1:** What category in OFPA does this substance fall under: (A) Does the substance
219 contain an active ingredient in any of the following categories: copper and sulfur compounds, toxins
220 derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treated seed, vitamins and
221 minerals; livestock parasiticides and medicines and production aids including netting, tree wraps and
222 seals, insect traps, sticky barriers, row covers, and equipment cleansers? (B) Is the substance a synthetic
223 inert ingredient that is not classified by the EPA as inert of toxicological concern (i.e., EPA List 4 inert)
224 (7 U.S.C. § 6517(c)(1)(B)(ii))? Is the synthetic substance an inert ingredient which is not on EPA List 4,
225 but is exempt from a requirement of a tolerance, per 40 CFR part 180?

226

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

229

230 (B). Lignin sulfonate is a synthetic inert ingredient that is not classified by EPA as an inert of
231 toxicological concern. Lignin sulfonate (and the lignosulfonate salts) are exempt from the
232 requirement of a tolerance under 40 CFR parts 180.910 and 180.930.
233

234 **Evaluation Question #2: Describe the most prevalent processes used to manufacture or formulate the**
235 **petitioned substance. Further, describe any chemical change that may occur during manufacture or**
236 **formulation of the petitioned substance when this substance is extracted from naturally occurring plant,**
237 **animal, or mineral sources (7 U.S.C. § 6502 (21)).**
238

239 Lignin sulfonates are produced from the process of sulfite chemical pulping. Sulfite pulping involves
240 cooking softwood chips under pressure in sulfur dioxide-containing cooking liquors. When the cooking
241 process is complete, sulfonated lignin is collected as a liquid by-product in the spent liquor, while the pulp
242 is used for paper production. The lignin sulfonates that result from the spent liquor of the sulfite pulping
243 process must be further purified to remove excess sugars. This is done by fermentation of the liquor,
244 followed by heating to remove the alcohol generated. The resulting lignin sulfonate polymers can have
245 high molecular weights ranging from less than 1,000 to more than 100,000 daltons (Zhor and Bremner,
246 1999; Westvaco Corp., 1987).
247

248 Lignin sulfonates may also be obtained from the Kraft pulping process; these are referred to as Kraft
249 lignins. Kraft pulping is similar to sulfite pulping, but involves treating the wood at high temperature and
250 pressure in a water solution containing sodium sulfide and sodium hydroxide. This process dissolves
251 lignin into a soluble salt which dissolves in the pulping liquor. The lignin is removed by precipitation from
252 the liquor using carbon dioxide (CO₂). The Kraft lignins must then be sulfonated after extraction by
253 reacting the material with bisulfate or a sulfite compound (Gundersen and Sjoblom, 1999; U.S. EPA, 1990).
254

255 A third pulping process, acid sulfite pulping, is similar to Kraft pulping, but different chemicals are used.
256 Sulfurous acid, used in place of sodium hydroxide, is combined with sodium, magnesium, calcium, or
257 ammonium bisulfite. After the cooking is complete, the pulp is separated from the spent liquor, which
258 may then be treated to obtain various chemical materials (U.S. EPA, 1990).
259

260 **Evaluation Question #3: Is the substance synthetic? Discuss whether the petitioned substance is**
261 **formulated or manufactured by a chemical process, or created by naturally occurring biological**
262 **processes (7 U.S.C. § 6502 (21)).**
263

264 Lignin exists naturally in all woody plants as a structural and strengthening component. Because lignin is
265 integrated into the plant cell wall, there are no natural processes that liberate lignin other than natural
266 decomposition of wood by microorganisms. Lignin sulfonates are produced from the application of
267 pressure and heat to wood in the presence of sulfur dioxide or by the addition of alkali and various acids
268 and sulfates, as described under Evaluation Question #2. These are not naturally-occurring processes.
269 Therefore, lignin sulfonates are synthetic (U.S. EPA, 1990; Gundersen and Sjoblom, 1999).
270

271 **Evaluation Question #4: Describe the persistence or concentration of the petitioned substance and/or its**
272 **by-products in the environment (7 U.S.C. § 6518 (m) (2)).**
273

274 Lignosulfonates discharged into water bodies may cause foaming and discoloration. Due to their high
275 biological oxygen demand (BOD) during breakdown in water, lignosulfonates will remove dissolved
276 oxygen from waterways in amounts that may be harmful to aquatic organisms (CPWA, 2005). Little
277 additional information is available in the published literature on the degradation pathways for
278 lignosulfonates in water.
279

280 The half-life of lignosulfonates in soil, as evidenced by the loss of sulfates or sulfonic acid groups, is up to
281 one year. Soil microorganisms, enzymatic reactions, and ultraviolet (UV) radiation contribute to the
282 breakdown of lignosulfonates. The structure of lignosulfonates may be altered by wood-rotting fungi, with

283 polymerization being the main pathway, based on a decrease in phenolic hydroxyl groups (Selin et al.,
284 1975). Laccase, an enzyme produced by fungi, increased degradation of lignosulfonates to low-molecular
285 weight fractions under laboratory conditions (Cho et al., 2004). In addition to microbial decomposition,
286 enzymatic oxidative reactions contribute to the early breakdown process of lignosulfonates. Light (UV
287 radiation) also hastens the degradation of lignosulfonates by creating radicals capable of degrading the
288 lignosulfonate molecular structure. This breakdown process yields lower molecular weight lignosulfonate
289 fragments and CO₂. The CO₂ may account for 15–20% of the original organic carbon. As lignosulfonates
290 degrade, they become more susceptible to further degradation by microbial populations. Due to the
291 complex and heterogeneous structures of lignosulfonates, detailed information about breakdown products
292 is difficult to describe (Lauten et al., 2010). Given that lignin is a naturally-occurring component of wood,
293 once the sulfonic acid groups have been cleaved, the lignin that remains would likely be broken down in a
294 manner very similar to that of rotting wood.

295

296 **Evaluation Question #5: Describe the toxicity and mode of action of the substance and of its**
297 **breakdown products and any contaminants. Describe the persistence and areas of concentration in the**
298 **environment of the substance and its breakdown products (7 U.S.C. § 6518 (m) (2)).**
299

300

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

312

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

318

319 In a 90-day study with Wistar rats dosed with calcium lignosulfonate in the diet at target doses of 0, 500,
320 1000, and 2000 mg/kg-day, the rats showed no adverse clinical signs or organ weight changes following
321 complete pathological evaluations. Test results for primary immune response in the rats were normal. The
322 only observed adverse effect was a dose-related increase in the incidence of histiocytosis (abnormal
323 increase in the number of immune cells) of the mesenteric lymph nodes in male and female rats, with no
324 observed histiocytosis in other lymph tissues. The Joint FAO/WHO Committee reviewed the finding of
325 histiocytosis and concluded that it does not represent an adverse effect, based on findings with other
326 compounds with similar properties (Munro and Baines, 2009).

327

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

332

333 Lignin sulfonates are soluble in water, so it is possible for dissolved lignosulfonates to enter waterways
334 through direct contamination or soil runoff. Lignosulfonates in water may be toxic to fish. A 48-hour LC₅₀
335 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

336 affect aquatic organisms through a decrease in available oxygen (CPWA, 2005; Jones and Mitchley, 2001).
337 Due to the acidic pH of lignosulfonates, large spills to waterways may also affect pH of waterways.

338
339 In the previous technical report (NOSB, 1995), a letter from the petitioner addresses concerns with dioxin as
340 a contaminant from the process of paper pulping. Dioxin is a highly-toxic contaminant that is considered a
341 likely human carcinogen (U.S. EPA, 2010c). The petitioner noted that dioxins are generally associated with
342 the Kraft pulping process, and that dioxins are produced as part of pulp bleaching. The petitioner
343 (Western Chemicals) noted that the Georgia-Pacific Corp. generates its lignosulfonates using the bisulfite
344 pulping process (NOSB, 1995). The petitioner also explained that the sulfite liquor, which contains the
345 lignosulfonates, is removed from the pulp before the bleaching process; thus, it is not likely that dioxins
346 would be found in the lignosulfonates generated from this process (NOSB, 1995). In addition, the
347 petitioner reported that they had analyzed their lignosulfonate products for dioxins and furans, and have
348 not detected the contaminants in their lignosulfonate products above the level of detection (NOSB, 1995).

349
350 Georgia-Pacific Lignosite® 100, 260, 431-H, and 458 have been classified as biodegradable, with a hazardous
351 decomposition product of sulfur dioxide (SO₂), which can adversely affect the respiratory system (Ash and
352 Ash, 2004; U.S. EPA, 2011b). Selin et al. (1975) commented on the recalcitrant (resistant to degradation)
353 nature of lignosulfonates, but also showed that many wood-decomposing microbes could break down
354 lignosulfonates. As described in the Action of the Substance section, lignin sulfonates bind strongly to
355 smaller particles in the soil or water. Once adsorbed to the soil, lignosulfonates will be degraded by soil
356 microorganisms. Lignosulfonates may persist for six months to one year when used for dust suppression
357 before they break down (CPWA, 2005; Selin et al., 1975).

358
359 **Evaluation Question #6: Describe any environmental contamination that could result from the**
360 **petitioned substance's manufacture, use, misuse, or disposal (7 U.S.C. § 6518 (m) (3)).**

361
362 Manufacture: Spent sulfite liquors from the paper pulping process contain lignin sulfonate. Before the
363 widespread use of lignin sulfonates, these liquors were treated as waste from the sulfate pulping process
364 and discarded or burned for energy recovery. Given that lignin sulfonate is recovered from waste
365 products of the paper pulp industry after manufacture, the likelihood of environmental contamination
366 from its manufacture is reduced. However, there is still the possibility that spills of effluent from paper
367 pulping operations could contribute large amounts of lignin sulfonate to soils, nearby waterways, or
368 environmentally-sensitive areas.

369
370 Use: Lignin sulfonates used as dust suppressants or in chelates applied as plant nutrients to the soil may
371 contaminate waterways via runoff following a rain event. The primary concern regarding lignin sulfonates
372 in waterways is their high BOD upon decomposition. This causes removal of dissolved oxygen from the
373 water and impacts aquatic organisms (CPWA, 2005).

374
375 Misuse: Dust explosions may occur if finely-divided lignin sulfonate is mixed with air in the presence of
376 an ignition source. Excessive accumulation of dust should be avoided to help prevent explosions (Georgia-
377 Pacific West, Inc., 2000). Decomposition of lignin sulfonate can release SO₂, which is an eye and airway
378 irritant (Sullivan and Krieger, 1992; Georgia-Pacific West, Inc., 2000). Excessive amounts of lignin sulfonate
379 applied to roads for dust suppression or large amounts applied just prior to rainfall events may increase
380 the potential for lignin sulfonate to runoff to waterways.

381
382 Disposal: Lignin sulfonate-treated dump water for pear processing may need to be processed in a
383 treatment system before its disposal. The goal for treatment of these waters is reduction in BOD to a level
384 that does not impact aquatic life (McLellan and Padilla-Zakour, 2005). Untreated dump water could
385 adversely affect aquatic organisms by competing for dissolved oxygen. In the case of spills or accidents
386 involving lignin sulfonate, the area should be washed with water to dilute the spill (Georgia-Pacific West,
387 Inc., 2000). To the extent possible, care should be taken to ensure that wastewater does not flow directly to
388 water bodies. For spills, waste disposal methods include customary procedures for industrial waste
389 treatment (Georgia-Pacific West, Inc., 2000). Spills or releases of lignin sulfonate are not subject to the

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

392
393 Other: Lignin sulfonates have been investigated for their potential role as chelating agents for the
394 complexation of metal ions, including copper, magnesium, and mercury, for the purpose of environmental
395 remediation. The biodegradability and relatively inexpensive nature of the lignin sulfonates were cited as
396 factors that support their use in remediation (Garcia-Valls et al., 2001). In a report on lignin and its uses by
397 USDA, lignosulfonates were discussed as treatments for food waste from milk processing plants and meat
398 or fish canneries. The lignosulfonate complexes form a precipitate which was then added to animal feed.
399 This application prevented some of the food waste from these operations from entering waterways (USDA,
400 1969).

401
402 **Evaluation Question #7: Describe any known chemical interactions between the petitioned substance**
403 **and other substances used in organic crop or livestock production or handling. Describe any**
404 **environmental or human health effects from these chemical interactions (7 U.S.C. § 6518 (m) (1)).**
405

406 Lignin sulfonates are intended to be used as chelating agents for plant nutrients, dust suppressants, and
407 emulsifiers. By virtue of their intended use, chemical interactions of lignin sulfonates with other
408 substances would be expected. However, lignin sulfonates are generally nonreactive by nature. When
409 used as emulsifiers, lignin sulfonates keep chemical mixtures dispersed in solution by limiting interaction
410 between the two constituents of the mixture (Gundersen and Sjoblom, 1999). When lignin sulfonates come
411 into contact with small soil particles through their use as dust suppressants or chelating agents, the soil
412 particles are adsorbed to the lignin sulfonate due to the presence of polar and non-polar areas on the
413 surface of the lignin molecule. These interactions do not generally result in chemical change but are mostly
414 limited to a physical binding and adsorption. The exception to this is the corrosion of aluminum and its
415 alloys by lignin sulfonates when the material is used as a dust suppressant. This reactivity is of concern
416 due to the prevalence of aluminum or alloy wheels, which can be corroded by the lignin sulfonate as cars
417 with this type of wheel drive over treated roads. Mixing the lignin sulfonate with calcium carbonate in
418 slurry neutralizes the acidic lignin sulfonate and decreases the reaction with aluminum (CPWA, 2005).
419

420 Information on environmental or human health effects from chemical interactions with lignin sulfonate
421 was not available. As a chelating agent, lignin sulfonates could serve to reduce environmental health
422 effects and potential toxicity to humans from exposure to the free metal ions (Garcia-Valls et al., 2001). The
423 biodegradability and relatively inexpensive nature of the lignin sulfonates were cited as factors supporting
424 their use in remediation (see Specific Uses and Historic Use sections and the response to Evaluation
425 Question #6).
426

427 **Evaluation Question #8: Describe any effects of the petitioned substance on biological or chemical**
428 **interactions in the agro-ecosystem, including physiological effects on soil organisms (including the salt**
429 **index and solubility of the soil) crops, and livestock (7 U.S.C. § 6518 (m) (5)).**
430

431 Lignin sulfonates break down by physical or microbiological processes, but may persist in the soil up to
432 one year. Lignin sulfonates are unlikely to accumulate in soil unless they are applied very frequently.
433 Breakdown of lignin sulfonate occurs in part because lignin sulfonate is used as a carbon source by a
434 variety of wood-decaying microorganisms. It is therefore likely that large amounts of lignin sulfonate
435 applied to soils could stimulate soil microbial activity.
436

437 When lignin sulfonate decomposes in soil, sulfates, sulfonic acid groups, and CO₂ are liberated (Selin et al.,
438 1975). The breakdown of a large amount of lignin sulfonate in the soil (resulting in the release of additional
439 CO₂) could acidify the soil (CO₂ forms carbonic acid in the presence of water). Changes in pH due to the
440 addition of large amounts lignin sulfonate could adversely affect plants and soil organisms, but these
441 effects have not been quantified in the published literature.
442

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

451
452 When lignin sulfonates are discharged to waterways, their decomposition removes dissolved oxygen from
453 water. The lack of dissolved oxygen is harmful to aquatic organisms and, depending on the amount of
454 lignin sulfonates that is discharged, can have a negative impact on aquatic organisms to varying degrees.
455 Lignosulfonates are corrosive to aluminum and aluminum alloys in the absence of calcium carbonate. If
456 the corrosion of aluminum or its alloys occurs as a result of lignosulfonate application to roadways, then
457 contamination of nearby waterways with the corrosion products could result. If the lignosulfonate is
458 applied with calcium carbonate in slurry, the effect is neutralized (CPWA, 2005).

459
460 **Evaluation Question #9: Discuss and summarize findings on whether the petitioned substance may be**
461 **harmful to the environment (7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i)).**

462
463 As discussed in Evaluation Questions #4 and #6, lignin sulfonates used as dust suppressants or in chelates
464 applied as plant nutrients to the soil may contaminate waterways via runoff following a rain event. When
465 used as a flotation aid for dump tanks in pear processing, lignin sulfonates may be discharged to
466 waterways due to improper disposal of the dump water (normal disposal would require treatment of the
467 processing water before disposal). Accidental spills of lignin sulfonate may also result in contamination of
468 waterways. Lignin sulfonates readily dissolve in water (forming acids) and may decrease the pH of waters
469 they contaminate. The severity of this effect will depend on the amount discharged and the characteristics
470 of the receiving water body. Due to their high BOD during decomposition, lignosulfonates will remove
471 dissolved oxygen from waterways in amounts that may adversely affect aquatic organisms such as fish or
472 aquatic invertebrates (CPWA, 2005).

473
474 As discussed above for Evaluation Question #8, lignin sulfonates decompose by physical or
475 microbiological processes, but may persist in the soil in varying amounts at up to one year. However,
476 significant amounts of lignin sulfonates are unlikely to accumulate in agricultural soils unless they are
477 applied frequently.

478
479 Lignin sulfonate may be applied to control road dust. If these applications are frequent and are made
480 during very dry periods, it may lead to an accumulation of lignin sulfonates in the road bed. Runoff flows
481 along the ground surface could transfer the accumulated lignin sulfonate to nearby terrestrial systems or
482 waterways. Large amounts of lignin sulfonates in agricultural soils could cause a decrease in pH (due to
483 decomposition of lignin sulfonate, release of carbon dioxide and sulfur dioxide, and formation of acids)
484 (see Evaluation Question #8). The acidification of the soil could adversely affect crops and soil
485 microorganisms depending on the extent of acidification.

486
487 **Evaluation Question #10: Describe and summarize any reported effects upon human health from use of**
488 **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**
489 **(m) (4)).**

490
491 The U.S. EPA issued an exemption from the requirement of a tolerance for lignin sulfonates when they are
492 used as inert ingredients pre- and post-harvest in agricultural production. This exemption is based on the
493 conclusion that there is a “...reasonable certainty that no harm will result...” to the general public, infants,
494 and children from aggregate exposures (includes all dietary, drinking water, and non-occupational
495 exposures) to lignosulfonates, as defined by the Federal Food, Drug, and Cosmetic Act (FFDCA) and the
496 Food Quality Protection Act of 1996 (FQPA) (U.S. EPA, 2011a; Federal Register, 2005).

497

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

501

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

505

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

514

515 According to a survey from 1998 of pear packers in the western U.S., about 70 percent of packing houses
516 used a form of lignin sulfonate for pear flotation (Sugar, 2002). However, a major source of lignin sulfonate
517 in the Pacific Northwest closed prior to 2001, forcing growers to evaluate other alternatives for flotation
518 (Sugar, 2002). Two new products were evaluated in 2001 by researchers at Oregon State University – K-
519 Float (potassium carbonate) and Xeda F (potassium phosphate and potassium pyrophosphate) – along with
520 sodium carbonate, calcium chloride, and sodium sulfate for their use in pear flotation. These products
521 were evaluated at the Southern Oregon Research and Extension Center in Medford, OR, and the findings
522 were reported at the Washington Tree Fruit Postharvest Conference on March 12th and 13th, 2002, in
523 Yakima, WA. All tested products performed in a manner similar to lignin sulfonate to raise the density of
524 water in dump tank solutions and allow pears to float for easier and less-damaging processing. When used
525 in combination with Steri-Seal (an antimicrobial agent) the “relatively low” pH solutions containing Xeda
526 F, calcium chloride, and sodium sulfate were more likely to cause fruit burn than the “relatively high” pH
527 solutions including lignin sulfonate, sodium carbonate, and K-Float (Sugar, 2002). Fruit burn is caused in
528 part by the increased availability of phenol that occurs at lower pH. For higher pH solutions, more Steri-
529 Seal had to be added to dump tanks to prevent fruit infection (Sugar, 2002). In practice, multiple materials
530 may be mixed at varying percentages in order to achieve the desired decrease in fruit injury and infection
531 rates (Sugar, 2002). In these tests, a mixture of Xeda F with Steri-Seal disinfectant at 1percent provided the
532 lowest gray mold infection rate (12 percent). However, all of the alternate treatments caused some degree
533 of fruit injury at increased dump tank temperature. The exception to the rule was lignin sulfonate, which
534 was found to lower pH levels, but also have a “safening” property for phenol injury at a low pH (Sugar,
535 2002).

536

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

543

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

548

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

551
552 **Pear Flotation:** Pear damage can occur throughout the harvest process, but one of the main sources of
553 damage is when the pears are dumped from bins during rapid unloading. Dry dumps from harvest bins to
554 packing bins can cause the most damage, whereas wet dumps (from a dry bin into a water-filled bin)
555 decrease the potential for fruit injury. Wet dumps also allow pears to more easily move onto conveyors
556 where they are inspected and packed. Due to the high density of pears, some are heavier than water.
557 Flotation salts, including lignin sulfonates, are sometimes added to increase dump water density and allow
558 the pears to float, thus reducing the chance for injury and increasing packing efficiency – a process called
559 an immersion dump. The fruit is then circulated in the dump water using a pump, which floats the fruit to
560 an elevator where it is rinsed and moved to a conveyor for packaging. The flotation salts could be left out
561 of the process and non-immersion water dumps could be used. To minimize damage in non-immersion
562 dumps from fruit-to-fruit injury, more time is required to allow fruit to move onto conveyors before
563 additional fruit is dumped. Additional steps to reduce fruit damage have also been proposed which
564 include using padded picking containers or plastic-lined wooden picking bins to reduce scuffing (Agar and
565 Mitcham, 2000).

566
567 **Dust Suppression:** Alternate methods of dust suppression from best management practices include:
568 vegetative cover (for non-traffic areas); mulch (including gravel mulch); sprinkling with water; spray-on
569 adhesives (including anionic asphalt emulsion, resin in water, and latex emulsion); applications of stone or
570 gravel to disturbed roads; barriers to control air currents; or surface roughening at angles perpendicular to
571 prevailing winds (U.S. EPA, 2006; Idaho DEQ, 2005). Most of these methods (with the exception of
572 adhesive applications and water sprays) do not involve applications similar to those used for lignin
573 sulfonate, but are physical manipulations of the landscape. Cost, available resources, level of control, and
574 the extent of the dust problem are factors that may affect the choice of dust control measures (U.S. EPA,
575 2006).

576
577 Researchers at Colorado State University evaluated three dust suppressants – calcium lignosulfonate,
578 magnesium chloride, and calcium chloride – for their effectiveness in reducing dust emissions from
579 unpaved roads (Sanders and Addo, 1993). Preliminary data analysis indicated that all suppressants
580 reduced the dust emitted compared to untreated roads (Sanders and Addo, 1993). Final data (Sanders and
581 Addo, 1993) showed that the aggregate loss of road height after one year was 5.18, 5.80, and 7.01 mm for
582 roads treated with magnesium chloride, calcium lignosulfonate, and calcium chloride, respectively
583 (Sanders and Addo, 2008). The untreated road showed an aggregate loss of 15.55 mm after one year.

584
585 **Micronutrient Fertilizer Chelates:** In addition to the use of allowed nonsynthetic chelates, soil fertility can
586 be managed in other ways. Naturally-occurring chelates in the soil include humates, fulvates, and organic
587 root exudates. Fulvates and humates are found naturally in most soils as the result of the decomposition of
588 organic matter. Management practices, including no-till farming or manure applications, can increase
589 organic matter in the soil and thereby increase the rate of naturally-occurring chelates (Jones and Jacobsen,
590 2009)

591
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