Q. What are lignosulfonates and where do they come from?

A. Lignosulfonates are complex polymers derived from trees. The wood from trees is composed mainly of three macromolecular components – cellulose, hemicellulose and lignin. In the sulfite pulping process, the lignins are sulfonated so they become water-soluble and thus can be separated from the insoluble cellulose. The soluble lignins are called lignosulfonates.

Q. What are lignosulfonates used for?

A. Lignosulfonates are extremely versatile and are used in a wide variety of industrial applications. While generally associated with dust control and surface stabilization for roads, they are used as binders, dispersants, emulsifiers and sequestrants in a host of products such as gypsum board, animal feed pellets and micronutrient systems.

Q. Are lignosulfonates “environmentally friendly?”

A. Extensive studies have been conducted to evaluate the effects of lignosulfonates on the environment. Results show that they are not harmful to plants, animals or aquatic life when properly manufactured and applied. Lignosulfonates have been used as a treatment for dirt roads in Europe and the U.S. since the 1920’s.

Q. Do lignosulfonates contain heavy metals?

A. Lignosulfonates are derived from wood and thus contain the metals that are naturally present in trees. The levels and types of metals vary depending upon the types of trees and the soil on which they were grown.

The amount of metals typically found in lignosulfonates is well below one part per million (ppm). The industry has voluntary standards for the levels of heavy metals in lignosulfonates.

Q. Do lignosulfonates contain dioxins?

A. Dioxins are occasionally associated with the pulp bleaching process used in the wood pulp industry. However, since lignosulfonates are removed from the pulp prior to bleaching, dioxins are not manufactured into the product.

(over)
However, just as with other substances, lignins can contain trace amounts of dioxins if they come into contact with dioxin-containing materials. The U.S. Environmental Protection Agency (EPA) reported in 1994 that the major source of dioxin is airborne contamination from incineration. Consequently, dioxins are practically ubiquitous.

Q. **Are lignosulfonates toxic?**

A. Lignins are no more toxic than table sugar. In other words, they are relatively harmless. Animal toxicity studies reveal that baking soda, table salt and Vitamin C all are significantly more toxic than lignins.

Perhaps the best testimony to the safety of lignosulfonates is the fact that the U.S. Food and Drug Administration has issued nine approvals for their use in food contact applications. They also approved for use as a pelletizing and binding aid in animal feeds.

Q. **Can lignosulfonates trigger asthma attacks?**

A. No, in fact, when used as a dust suppressant they can help to control particulate matter that might otherwise induce asthmatic symptoms.

Lignosulfonate solutions coat individual road particles with a then adhesive-like film that binds the particles together thereby controlling dust that might otherwise adversely affect asthmatics.

Q. **Can lignosulfonates decompose into sulfur?**

A. The sulfur bound in lignosulfonates is oxidized to sulfate – not sulfur – after application. There are no studies in the scientific literature citing sulfate as a causative factor in asthmatic reactions.
Aquatic Toxicity of 35% w/w TDS

Table 1: Aquatic toxicity of 35% w/w TDS

<table>
<thead>
<tr>
<th>Year of Examination at Bodycote</th>
<th>Tests</th>
<th>Concentration % v/v (95% confidence interval)</th>
</tr>
</thead>
<tbody>
<tr>
<td>April 2005</td>
<td>Microtox LC₅₀ 5 minutes</td>
<td>0.06 (0.04 - 0.08)</td>
</tr>
<tr>
<td></td>
<td>Daphnie LC₅₀ – 48 hours</td>
<td>0.13 (0.10 – 0.17)</td>
</tr>
<tr>
<td></td>
<td>Algae (IC₅₀ – 96 hours)</td>
<td>0.023 (0.018-0.027)</td>
</tr>
<tr>
<td></td>
<td>Fathead Minnows IC₅₀ – 7 days</td>
<td>0.017 (0.013 – 0.019)</td>
</tr>
<tr>
<td></td>
<td>Fathead Minnows LC₅₀ – 7 days</td>
<td>0.018 (0.016– 0.021)</td>
</tr>
<tr>
<td>April 2003</td>
<td>Microtox LC₅₀ 5 minutes</td>
<td>0.07 (0.06 - 0.09)</td>
</tr>
<tr>
<td></td>
<td>Daphnie LC₅₀ – 48 hours</td>
<td>0.18 (0.13 – 0.25)</td>
</tr>
<tr>
<td></td>
<td>Algae (IC₅₀ – 96 hours)</td>
<td>0.02 (0.017 – 0.023)</td>
</tr>
<tr>
<td></td>
<td>Fathead Minnows IC₅₀ – 7 days</td>
<td>0.039 (0.035 – 0.042)</td>
</tr>
<tr>
<td></td>
<td>Fathead Minnows LC₅₀ – 7 days</td>
<td>0.040 (0.035 – 0.047)</td>
</tr>
<tr>
<td>June 1999</td>
<td>Microtox LC₅₀ 5 minutes</td>
<td>0.117 (0.083 - 0.164)</td>
</tr>
<tr>
<td></td>
<td>Daphnie LC₅₀ – 48 hours</td>
<td>0.023 (0.004 – 0.125)</td>
</tr>
<tr>
<td></td>
<td>Algae (IC₅₀ – 96 hours)</td>
<td>0.09 (0.07 – 0.010)</td>
</tr>
<tr>
<td></td>
<td>Fathead Minnows IC₅₀ – 7 days</td>
<td>0.020 (0.018 – 0.022)</td>
</tr>
<tr>
<td></td>
<td>Fathead Minnows LC₅₀ – 7 days</td>
<td>0.021 (0.013 – 0.05)</td>
</tr>
</tbody>
</table>

Table 2; Typical BOD and COD concentrations of 52% w/w ammonium lignosulfonates

<table>
<thead>
<tr>
<th>Test</th>
<th>Concentration (g/L, 52% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD₅</td>
<td>87</td>
</tr>
<tr>
<td>COD</td>
<td>890</td>
</tr>
</tbody>
</table>
**Brief Summary of the Sulfite Pulping Process at Temiscaming**

**Raw materials**
Various wood species are selected to maximize the wood utilization from the forest. At Tembec, we generally segregate hardwoods from softwoods and cook them separately. Hardwoods include aspen, maple, or birch. Softwoods include spruce, jackpine, hemlock, red pine and white pine. Cooking chemicals are ammonia and sulfur dioxide in an acid solution with water.

**Pulping**
Tembec uses 11 batch digesters to cook wood into pulp. The cooking acid at pH less than 1.0 is pumped into the digesters at the beginning of the cook. The cooking acid is circulated through steam heated heat exchangers and returned to the digester continuously as the cooking temperature is raised to about 150 °C over 3-4 hours. Sulfur dioxide is relieved and recovered as needed to maintain the proper cooking pressure. The cook continues for 6-8 hours until the desired end point is reached. At the end of the cook, pressure is relieved to about 10 psi and the mixture of pulp and spent sulfite liquor is sent to the recovery system. The pulp fibre is separated from the spent sulfite liquor by pressing and washing stages. The spent sulfite liquor is recovered at about 10% solids concentration with a pH of 1.5.

Tembec produces about 500 tonnes per day of pulp and about 600 tonnes of dissolved solids. At 10% concentration this amounts to about 6000 cubic meters of weak spent sulfite liquor.

During pulping, the lignin in the wood is sulfonated and hydrolyzed. The lignin becomes soluble and remains in the spent sulfite liquor. Because the cooking acid is at low pH, hemicelluloses are hydrolyzed and dissolved also. This results in the presence of monomeric sugars (e.g. glucose, mannose, galactose, xylose and arabinose) in the weak liquor at total concentration of about 25% of the total solids.

**Liquor Recovery and Alcohol Fermentation**
The spent sulfite liquor is evaporated from 10% concentration to 20% solids by removing water and sulfur dioxide. This solution is cooled to 30 °C and neutralized to pH 5.5 with ammonia. Yeast is added continuously to the liquor and fermentation occurs. All of the 6 carbon sugars (glucose, etc.) are fermented to ethanol and CO₂. The alcohol is stripped from the liquor by distillation, purified and sold as industrial, food grade alcohol. The stripped liquor is returned to another set of evaporators where the solid concentration is increased to 50%. Approximately 1200 tonnes of 50% liquor is generated per day. About 75% of the heavy liquor is burned as fuel in our boilers. The remaining 25% of the total is sold.

**Lignin Products**
The 50% liquor is called heavy liquor and is the basis for our lignosulfonate operation. Sodium products are made from the ammonium lignosulfonate heavy liquor by adding caustic soda to the liquor in a stripping column. Ammonia is driven off, recovered and sent back to the pulp mill. We sell both hardwood and softwood products which have differences in their chemical and physical properties based on the structure of the lignin in the different wood species.
Lignosulfonate

Regulatory Information and Toxicity Data

U. S. FOOD AND DRUG ADMINISTRATION

Subject to the provisions of each section in the Code of Federal Regulations, Dust Control 50 is approved for the following uses (please consult CFR Section for full text and limitations that may apply):

21 CFR 172.715: Approved for use in or on food as dispersing agent and stabilizer in pesticides for certain food crops.

21 CFR 175.105: Approved for use in adhesives used on contact with foods.

21 CFR 176.170: Approved for use as components of coatings for paper and paperboard used in packaging, processing, transporting, at cetera, of food.


21 CFR 573.600: Approved for use in animal feed up to 4%.

Letter of Approval: Considered generally recognized as safe for use in flotation tanks for washing whole pears provided that the pears are subjected to a potable water rinse after leaving the flotation tank.

U. S. COAST GUARD AND MARITIME

46 CFR 150: Notice of compatibility with all cargo except sulfuric acid and isocyanates.

TOXICITY

LD$_{50}$ = 28.5 gms solids/kg in rats - "not toxic" by FHSA definition.

Not a skin or eye irritant by FASA definition.
Not listed as a carcinogen by IARC, NTP, OSHA or ACGIH.

CODE OF FEDERAL REGULATIONS

Subject to the provisions of each section, Dust Control 50 is approved for the following uses (please consult CFR Section for full text)

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21 CFR 573.600: Approved for use in animal feed up to 4%.

46 CFR 150: Notice of compatibility with all cargo except sulfuric acid and isocyanates.

46 CFR 153: May be carried in tank vessels having neither a Certificate of Inspection under Subchapter D (tank vessels) nor a Letter of Compliance under Part 153.

TOXICITY

LD$_{50}$ = 28.5 gms solids/kg in rats - "not toxic" by FHSA definition.

Not a skin or eye irritant by FASA definition.

Exposure of six rats to 198 mg/m$^3$ of Dust Control 50 dust for four hours resulted in neither mortality nor observed signs of toxicity.

96-hour LC$_{50}$ Static Bioassay of Dust Control 50 liquor gave a lethal concentration (LC$_{50}$) of 4250 mg/l for juvenile rainbow trout.
OTHER

ACGIH: No threshold limit value (TLV+) established by American Conference of Governmental Industrial Hygienists

OSHA: No permissible exposure level (PEL) established by OSHA.

TSCA: Registered under Toxic Substances Control Act, initial inventory, CAS # 68131-32-8.

USDA: USDA self-certification (9 CRF 317.20); is FDA approved.

Dust Control 50 has been approved by the U.S Forest Service for use on roads for dust abatement.
Toxicology

Toxicological studies have shown that lignosulfonates are nontoxic. The United States Food and Drug Administration issued regulations for the safe use of lignosulfonates in the manufacture and processing of a wide variety of food and in related food packaging applications. These include:

1. As adjuvants in pesticide chemical formulations exempt from the requirements of tolerance when applied pre- or post-harvest: 21 CFR 182.99, 40 CFR 180.910 and 180.920 [formerly known as 40 CFR 180.1001(e) and 40 CFR 180.1001(d)].

2. As dispersants or stabilizers in pesticides applied pre- or post-harvest to bananas: 21 CFR 172.715.

3. In animal feed as: (a) Pelleting and/or binding aid, limit of 4%; (b) Surfactant in molasses, limit of 11%; (c) Source of metabolizable energy, limit of 4%; 21 CFR 573.600.


5. As components of food packaging adhesives: 21 CFR 175.105.

6. As components of paper or paperboard used in direct contact with moist, fatty or dry food. This includes use in wax and rosin sizes, alkyl ketene dimers and animal glues: 21 CFR 176.170, 178.3120, 176.120, 176.180.

7. As components of closure sealing gaskets a limit of 0.2% sodium lignosulfonate: 21 CFR 177.1210.

8. As a boiler water additive used in the preparation of steam that will contact food: 21 CFR 173.310.

9. Exempted from requirements of a tolerance when used as ingredients in pesticide formulations applied to animals: 40 CFR 180.930 [formerly 40 CFR 180.1001(e)].

10. Substances generally recognized as safe: 21 CFR 582.99.