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INFOMINE market research group

Lignosulfonates
Production, Market and Forecast in Russia

Sample PDF

Moscow
April, 2016

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ANNOTATION

This report is the first edition of research of the lignosulfonates market in Russia.

The purpose of the study is an analysis of the Russian market of technical lignosulfonates.

The object of the study are technical lignosulfonates (LST), liquid and powder, as well as the products of their processing.

This work is a **desk study**. As **information sources**, we used data of Rosstat, Federal Customs Service of Russia, railway statistics, sectoral and regional press, annual and quarterly reports of issuers of securities, and web-sites of producers of lignosulfonates.

The **chronological scope of the study**: 2011-2015, forecast - 2016-2020.

Geography of research: the Russian Federation - a comprehensive detailed analysis of the market.

The report consists of 6 chapters, contains 117 pages, including 48 Tables, 29 Figures and 1 Appendix.

The **first chapter** of the report describes the technology of production of lignosulfonates (LST), the requirements for the product quality, as well as the scope of application of lignosulfonates and products of their processing.

The **second chapter** is devoted to the production of lignosulfonates in Russia. This section presents data on volumes of the lignosulfonates production by Russian enterprises in 2011-2015, and describes the main producers of LST. The chapter presents estimates of manufacture of products of processing of LST in Russia and describes the main enterprises-processors.

The **third chapter** analyzes the Russian foreign trade operations with lignosulfonates and products of their processing for the period of 2011-2015. It presents data on volumes of exports and imports of the products, estimates the commodity and regional pattern of supplies.

The **fourth chapter** is devoted to analysis of prices on lignosulfonates. This section provides an overview of the export prices of LST and products of their processing, as well as gives the price of LST on the domestic market.

The **fifth chapter** of the report is devoted to the consumption of lignosulfonates; it gives the supply-demand balance of the product in Russia. This section also shows the sectoral structure of consumption, describes the main industrial applications and the largest enterprises-consumers of LST.

The **sixth chapter** of the report presents the forecast of development of the market of lignosulfonates until 2020, taking into account the forecast of development of the consuming industries.

The **Appendix** presents contact information on producers and processors of lignosulfonates in Russia.

The target audience of the research:

- Participants of the lignosulfonates market - producers, consumers, and traders;
- Potential investors.

The present study claims to be the **reference tool** for marketing services and for experts making management decisions, who work in the market of the pulp and paper industry.

Introduction

Liquid and powder technical lignosulfonates are a byproduct of the pulp and paper industry.

Lignosulfonates are water-soluble sulfonated derivatives of lignin, formed during the sulfite process of delignification of timber. Chemically, lignosulfonates are sodium salts of lignosulfonic acids with an admixture of reducing and mineral substances.

A sulfite liquor is an aqueous solution of many organic and inorganic substances, which pass into solution in the sulfite pulp cooking. The task of disposing of this waste is one of the most acute problems of the pulp and paper industry.

Lignosulfonates are a valuable byproduct of the sulfite delignification of wood. The decree of the President of the Russian Federation, dated July 7, 2011, # 899, approves the study of applications of lignosulfonate as one of priority areas of science, technology and engineering in the Russian Federation in terms of environmental management. It also corresponds to the NArFU development program for 2010-2020 with regard to the integrated use of biological resources, as well as protection and preservation of the environment.

The direct use of lignosulfonates in the various sectors of the economy is due to their physico-chemical properties: they are adhesives, binders, surfactants, etc.

Technical lignosulfonates found the use:

- As a plasticizer of cement and concrete;
- As a reagent for regulating the basic parameters of drilling fluids for the oil and gas wells;
- As a reagent for the flotation of ores;
- As a binder in the production of molding and core sand mixtures in iron, steel and non-ferrous castings;
- During the agglomeration of ferrous metal ores; in the manufacture of refractories; and during briquetting;
- As lubricants and cutting fluids during the hot stamping and forging, as a foaming agent in the acid pickling of metals;
- As a sizing agent for cellulose bases in the textile industry;
- During the granulation of carbon black and porous fillers made of bulk powder materials and batch mixtures;
- As a dispersant and a suspension stabilizer in the production of crop protection chemicals;
- As feedstock and a dispersant in the manufacture of synthetic tanning agents;
- For the manufacture of chipboard, fiberboard and plywood.

1. Production technology of LST (lignosulfonates technical) and requirements for the product quality. Applications of lignosulfonates. Products of the LST processing

The spent sulfite cooking liquor contains 8-12% of a dry matter, which is by about 90% by weight accounted for organic materials - wood processing products. Organic substances are presented primarily by carbohydrates (28-32% - for softwood and 38-42% - for hardwood), by lignosulfonates (55-60% - for softwood, 38-42% - for hardwood), and by organic acids and their salts (11-12% - for softwood, 23-26% - for hardwood). There are two ways of disposing of these substances. The first method includes the bioprocessing of carbohydrates and organic acids and the production of technical lignosulfonates, the second - the regeneration of cooking chemicals and the heat production.

The biochemical processing of spent cooking liquors, depending on the composition of monosaccharides, is carried out on the alcohol-yeast or yeast factories. The alcohol-yeast production initially utilized only hexoses undergoing the alcoholic fermentation. The residue after distilling off the alcohol, the so-called sulfite alcohol stillage, containing pentose sugars and organic acids, is used as a medium for growing the fodder yeast. Another way of the biochemical processing of liquors is the growing of yeast microorganisms having an ability to metabolize hexoses, pentoses, and many organic acids.

During the biochemical processing of sulfite liquors, the following products are released per 1 ton of cellulose from the spruce wood in the alcohol-yeast production - 75-95 dm^3 of 95% ethyl alcohol, 30-35 kg of the fodder protein yeast, about 30 kg of the liquid carbon dioxide; in the production of yeast - 90-110 kg of the fodder protein yeast. With a substantial increase in the pulp yield, the first scheme becomes less economical due to the fixation of glucomannan in the solid residue, and it is advisable to process the spent liquor only into the fodder yeast.

Technical lignosulfonates are obtained by concentrating the solution after the stage of production of ethanol (a sulfite-alcohol mash) or yeast (a sulfite-yeast mash). Solids (6-9%) of the sulfite yeast mash consists essentially of lignosulfonates, while the sulfite-alcohol mash may contain up to 1% of pentose monosaccharides.

Chemically lignosulfonates are complex compounds of phenylpropane derivatives with ester, acetal and carbon-carbon bonds, thus being the modified lignins.

Technical lignosulfonates are produced as liquids (with the solids content in different grades of product not less than 46, 47 and 50%), solids (at least 76%) and powders.

The technological process of the lignosulfonates production comprises the following steps:

1. Preparation and submission of the coolant in the spray dryer.
2. Feed of a liquid concentrate to the spray dryer.

3. Drying of the liquid concentrate.
4. Cleaning of the exhaust flue gases and their removal by an exhaust fan.
5. Pneumatic transport of the finished powder to packaging.
6. Packaging, storage and transportation of powder.

The mash before the feeding for a dryer is evaporated to dryness of about 24-30%, 40%, and then it is dried at 500°C in a flue gas stream containing no ash constituents. The liquid concentrate after the evaporation with a mass fraction of solids of 24-30% is taken from the evaporation unit and fed to the tank, located in the warehouse of liquid lignosulfonates, and then pumped to a receiving tank, located in the furnace section. In order to reduce the rate of corrosion of the dryer and the pollution of environment, sodium hydroxide is added to lignosulfonates to increase pH to 5-8 directly in the warehouse. The liquid concentrate from the container in an amount of 11.3-19.2 m^3/h is fed to the dryer. Before the dryer, the lignosulfonate solution is fed to the filters where it is cleaned from mechanical impurities larger than 1 mm. Filters work in shift. Switching from one filter to another must be carried out every shift or at when it is clogged. The clogged filter is cleaned with water. Tap water is washed down the drain. If necessary, the filter is cleaned via a removable cover.

After purification, lignosulfonates are fed to a spray dryer, which has the mechanism for spraying the lignosulfonate solution to the smallest particles in the spray dryer chamber. The dispersed to a fine state liquid concentrate gets into the coolant stream (a mixture of flue gases and air). Hot flue gases, coming into contact with a finely dispersed suspension, dry it to a solids content 92-96%. The basic amount of the dried concentrate (70%) is deposited in the conical part of the spray dryer, the remaining 30% of the powder go with the exhaust flue gases. Some lignosulfonate particles may be adhering to the walls of the drying chamber. As a result, smoldering pockets can occur in the dryer body and on the ducts. Therefore, vibrators, mounted on the outside of the dryer chamber, are periodically turned on according to a specified program to clean the walls of the drying chamber from the deposited particles of lignosulfonates. The coolant, leaving the drying chamber, carries with it up to 30% of the dried product. The dry and wet methods of cleaning of the coolant are provided to capture the powder particles. Spent flue gases from the drying chamber with a temperature of 90-120°C are fed into the separation group of cyclones, where they undergo the dry cleaning. Cyclones are included into two parallel groups of six pieces each. The powder, caught in cyclones, is directed by feeders into a pipeline for suplying the deposited in the drier powder to the discharge cyclone. The coolant then passes the wet wiping to reduce losses of lignosulfonates.

The powdered commodity lignosulfonate with the humidity of no more than 8% is fed from the cone dryer and a group of cyclones of dry cleaning to the discharge cyclone. The transport of lignosulfonate is carried out due to the vacuum created by the blowers. In the discharge cyclone, the powder is separated from the air stream. After the cyclone, the powder enters the feeding bin. The feeding bin is equipped with a vertical agitator. Then the powder by gravity goes to a packaging machine for loading into bags. Lignosulfonates are packaged in 20-25 kg into the wet strength paper bags. The filled bags are sent by a conveyor belt to the finished product warehouse, where they are manually stacked on pallets. The site of packaging is equipped with the necessary dust cleaning system. Warehouses should be closed, dry, and have a natural ventilation.

Technical lignosulfonates are produced according to the technical standard TU 2455-028-00279580-2004 (Table 1).

Table 1. Characteristics of technical lignosulfonates

<table>
<tr><th rowspan="2">Characteristic</th><th colspan="6">Grade</th></tr>
<tr><th>A</th><th>B</th><th>C</th><th>D</th><th>E</th><th>T</th></tr>
<tr><td>Content of dry substances, wt. %, at least</td><td>47</td><td>47</td><td>47</td><td>46</td><td>47</td><td>76</td></tr>
<tr><td>Content of ash in dry substances, wt. %, at most</td><td>18</td><td>25</td><td>22</td><td>5</td><td>not specified</td><td>18</td></tr>
<tr><td>Content of water insoluble substances, wt. % to total mass, at most</td><td></td><td></td><td>0.8</td><td>0.8</td><td>1.3</td><td>1.1</td></tr>
<tr><td>pH of 20% aqueous solution, at least</td><td>4.4</td><td>6.0</td><td>4.5</td><td>4.5</td><td>4.0</td><td>4.5</td></tr>
<tr><td>Density, kg/m^3, at least</td><td>-</td><td>-</td><td>1240</td><td colspan="3">not specified</td></tr>
<tr><td>Content of CaO, wt. %, at most</td><td colspan="3">not specified</td><td>0,8</td><td colspan="2">not specified</td></tr>
<tr><td>Content of dissolved substances, wt. %, to the mass of dry substances, at most</td><td colspan="3">not specified</td><td>12</td><td colspan="2">not specified</td></tr>
</table>

Note: A – lignosulfonates with improved binding properties, B - lignosulfonates neutralized for the production of carbon black, C - general purposes lignosulfonates, D - ammonium lignosulfonates for tanning, E - lignosulfonates for the cement industry, T - solid lignosulfonates of general purposes

Technical liquid lignosulfonates are shipped in railway tank cars with a bottom discharge, tank trucks, barrels and other containers.

Technical powder lignosulfonates are packed in:

- 4-layer paper bags according to GOST 2226 of the brand PM with a gated valve (the weight of at most 20 kg);
- Soft polypropylene containers, woven plastic, for bulk products with a lower unloading hatch of the type MKR with polyethylene liners weighing at most 450 kg;
- Soft polypropylene containers ("big bags") of the type MKP of the weight of at most 650 kg.

In terms of the impact on the human body, technical lignosulfonates are low-hazard substances (the hazard class 4 according to GOST 12.1.007). Technical lignosulfonates do not have the skin-resorptive, local irritant and allergic effects, they are the low toxicity products. Technical lignosulfonates are fireproof and explosion-proof. By their fire danger, their production refers to the "D" category.

The disposal of lignosulfonates can be divided into two main areas: a direct use and chemical processing.

Interest in technical lignosulfonates are primarily due to their high surface activity, thank to which they can be used as additives in various industries.

In the ***production of concrete***, additives based on lignosulfonates belong to hydrophilizing plasticizers. Their use decreases the separation of a concrete mix, the cement consumption is reduced by 8-10%, the density of the concrete mix increases and the curing speed slows down.

In cement or concrete mixtures, raw lignosulfonates additives are introduced in an amount of 0.15-0.20%, and superplasticizers are required in the amount of 0.5-2.0% by weight of a dry cement. When replacing superplasticizers with lignosulfonates the concrete strength increases by 20-25%, the cold resistance - by 3-4 times, and the cost of the mixture dramatically decreases with the addition of a small amount of lignosulfonates due to their adsorption on a surface of a solid phase. The use of lignosulfonates reduces the humidity of a raw slurry while maintaining its fluidity, which increases the furnace productivity and reduces the specific fuel consumption for the clinker calcination.

Technical lignosulfonates are used as a binder in the manufacture of molding and core mixtures for the ***iron, non-ferrous and steel casting***. At the same time, they replace some scarce and toxic materials: phenolic alcohols, urea-formaldehyde and phenol-formaldehyde resins. The use of binders based on lignosulfonates reduces the cost of suitable raw materials, increases the strength of the rods, decreases their friability to 0.05-0.08%, lowers the temperature and reduces the heat curing time.

Due to their binding, adhesive and surface active properties, lignosulfonates are ***used in the manufacture of panels: chipboard, wood-fiber and mineral wool***. Since reinforcing additives are rather scarce, expensive and even toxic phenol-formaldehyde or urea-formaldehyde resins, then mixing in the manufacturing process of modified lignosulfonates (20-30%) and resins provides a combined binder. Thus, the toxicity of plates treated with the additive based lignosulfonates is reduced by 50%. The use of 40 kg/m^3 of lignosulfonates in the manufacture of mineral wool sharply declines the consumption of toxic phenolic alcohols and, consequently, significantly reduces harmful emissions. Moreover, products in this case are more durable and water-resistant.

Technical lignosulfonates can be widely used as a corrective additive in the ***manufacture of expanded clay gravel***.

The expanded clay gravel is the most common artificial porous filler of light structural concretes; it is obtained by the swelling clays by a rapid firing in rotary kilns. Corrective additives, introduced into the composition of clay raw materials, allows to intensify the process, increase the bloating of raw materials, reduce the density, and improve the strength of the expanded clay. The addition of sodium lignosulfonate in the amount of 12% by weight of the dry raw clay allows producing expanded clay pellets with a lowered density of 0.38-0.43 g/cm^3.

In the ***oil refining and oil-extracting industry*** in drilling oil and gas wells, lignosulfonates are used as a reagent for regulating the basic parameters of drilling fluids. Also, they are a component of gelling systems, which are low-viscosity solutions with a pH of 2.5-3.0. The gel formation results in a redistribution of filtration flows and their better regulation, the leveling of the injectivity profile of injection wells, restricting the water inflow in the processes, which in turn increases the oil recovery. The use of lignosulfonates in these systems is possible due to absorbent properties of surface-active additives.

Technical lignosulfonates are also used for strengthening different types of structures: drilling mines, wells, etc.

In the ***mining industry,*** technical lignosulfonates are used as ***a flotation reagent*** - a substance that allows to achieve an incomplete wetting of particles, i.e., various minerals and ores, thus allowing the flotation process. Due to the fact that the technical lignosulfonates are inexpensive flotation agents, and several thousand of them are known, the demand for these reactants increases.

In addition, the mining industry uses technical lignosulfonates to enhance the drill wells. They are added in the construction of various coatings and bases. In the production of non-ferrous metals, lignosulfonates are used as a flotation reagent and a ***binder for briquetting of a fine reactant feed***. They are widely used as a binder and plasticizer in the manufacture of iron and steel, at sintering the ore, at the acid etching and the metal hardening, etc.

In the chemical industry, lignosulfonates are used in the ***manufacture of pesticides and seed dressing*** - as a dispersant and a suspension stabilizer in the production of thr crop protection chemicals.

The main problem with lignosulfonates is a large heterogeneity of industrial products in the structure and properties caused by a type of raw material and the process conditions. Therefore, to obtain the standardized by properties materials, a certain preparation of industrial lignins is required, which increases the cost of these products. In this case, the chemical modification is difficult because of the three-dimensional structure of polymers and a steric hindrance to the action of the reagents.

In order to regulate and strengthen the surface-active properties of technical lignosulfonates, they are subjected to diverse modifications. Modifications use various techniques such as the separation of mineral impurities and carbohydrate conversion products, the membrane separation, which provide the more uniform by molecular weight fractions, as well as allow the introduction of various mineral and organic co-reactants.

By introducing electrolyte additives into technical lignosulfonates, it is possible to control the rheological characteristics of systems with their participation. A replacement of a cation or the addition of salts containing a trivalent cation or a cation of a higher valency (Fe, Al, Cr), allows to influence the molecular weight distribution to increase the content of a high molecular weight fraction, significantly increasing the limiting adsorption and the rate of its achievement. The use of chromium salts also contributes to the oxidation of hydroxyl groups to carboxyl groups, which are ionized in water at higher pH, thus increasing the surface activity of lignosulfonates. The effectiveness of lignosulfonates as surfactants is improved by an addition of amines and aminoalcohols, as well as oligomeric amine compounds.

An introduction of functionals groups, not inherent in the original lignosulfonates, the change of the content of hydroxyl and sulfonate groups, the use of various types of structure breaking actions, and on the contrary, the condensation reactions, allow a wide range of changing in the molecular weight distribution and a hydrophilic-lipophilic balance, significantly affecting the adsorption processes occurring in the interphase borders, and thus changing consumer properties of technical lignosulfonates.

Russian companies mainly work in two ways to modify lignosulfonates - through the production of plasticizing additives for concrete and reagents for drilling wells.

The following products based on LST are manufactured as concrete plasticizers:

- Lignopan B-3. This is a product made from fractionated lignosulfonates, inorganic salts of ethers of cellulose and copolymers of acrylic series. It has a stabilizing effect, reducing the plaster - and water separation;
- Lignosulfonate technical modified LSTM-2. It is a product of interaction of technical sodium lignosulfonate and water-soluble urea resin. It represents a viscous dark brown or dark yellow liquid, soluble in water.
- KhDSK 1 - a modification with a mechano-chemical treatment with alkali;
- KhDSK-3 - the same with the introduction of polyethylene glycols;
- NIL-20 - a treatment with the cement slurry;
- NIL-21 - an introduction of defoamers of propargyl alcohol;
- MLS - a condensation with formaldehyde;
- KBM - a fractionation of lignosulfonates with calcium hydroxide followed by treatment with ash.

The drilling reagent ***OkzilM*** is an aluminum-chromium containing, high-molecular compound on the basis of technical lignosulfonates, with a mass fraction of 3-valent chromium of up to 2.8%. This reagent is prepared by treating diluted solutions of lignosulfonates with sulfuric acid and potassium bichromate, followed by oxidation with sodium hydroxide, neutralization and drying of the product.

The drilling reagent ***Ferrochrome lignosulfonate (FXLS)*** is prepared by the action of sulfuric acid salts of chromium and iron on a hot sulfite-alcohol stillage. Resulting iron and chromium salts of lignosulfonic acids are soluble in water. With the increasing content in the aqueous solution of chromium cations, the reagent acquires the properties of a viscosity reducer, and with increasing concentrations of iron cations - the fluid loss properties. The drilling reagent FXLS is designed to reduce the viscosity, the fluid loss and a static shear stress of fresh and weakly mineralized drilling fluids, especially for high-temperature wells conditions (200°C). The ability to dramatically improve the thermal stability of the solution is due to the presence of chromium compounds, which are currently the most effective tool against the coagulating action of high temperatures, thanks to a special type of the chrome plating of the surface of the particles of the solid phase. The important advantage of FXLS is its ability to reduce the viscosity of the gypsum solutions, which differs favorably from other inhibiting solutions by a low alkalinity and a high temperature resistance and the applicability for regulating the properties of calcium chloride containing mud solutions.

Of a considerable interest is the experience of the preparation of binders based on technical lignosulfonates (LST) and lignin wastes for the production of thermal insulation materials. The commercial production of the insulation material - ***lignoperlite*** - is mastered on the basis of a lignin binder and perlite.

For production of lignoperlite, a binder has been studied. This binder is composed of lignosulfonates of the brand KBZh, phosphoric acid, phenolic alcohols, the urea-formaldehyde resin MF-17, and sodium ethylsiliconate (GKZh-10). The curing of the composition of lignosulfonates with orthophosphoric acid and the urea-formaldehyde resin was performed at 80°C. The filler is a non-expanded perlite.

According to its physical-mechanical and technological properties, lignoperlite is not inferior to effective insulating materials of this class. Lignoperlite is efficient as a thermofiller in single-layer lightweight aggregate concrete panels. This material can be used for a thermal insulation of hardware at temperatures up to 200°C.

One of the variants of the chemical recycling of lignosulfonates is the production of low molecular weight substances from macromolecules of lignin. Despite the large number of studies, the obtaining low molecular weight products from lignins is not a widely spread practice. On industrial scale, only ***vanillin*** (3-methoxy-4-hydroxybenzaldehyde) is manufactured from lignin. In nature, vanillin is found in the fruit of the tropical plant - vanilla. However, it is economically expedient to prepare it by the synthesis from guaiacol (o-methoxyphenol) or from lignin, by oxidizing lignosulfonates with oxygen in an alkaline medium. At present, the total volume of the annual production of vanillin is about 12,000 tons, and more than 70% of the material is obtained from lignosulfonates. The yield of vanillin according to the nature of lignosulfonates and conditions of oxidation is in the range of 6-12%.

Vanillin is widely used as a fragrance in perfumes and the cosmetic industry and as the flavor additive in the production of some foods. Additionally, vanillin is used in fine organic synthesis for medicines.

Currently, in Russia the production of vanillin from lignosulfonates is absent. Only one company, Syassky PPM, has a pilot plant for processing sulfite liquors of the pulp production with the capacity up to 30 tons/year, which in the years of reforms has been stopped due to the lack of competitiveness with the imported vanillin, mostly Norwegian and Polish, on the Russian market.