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Use of Lignosulfonates in Newsprint Paper Production

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Abstract—A short overview of the most prospective applications of industrial lignosulfonates in various industries, such as newsprint paper production, is presented. Lignosulfonates can be utilized in technological processes in various forms, including (1) forms immobilized by paper components and (2) chemically modified forms used as functional additives to the composition of paper-making stock.

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Lignosulfonates are byproducts from the production of pulp from raw wood using the sulfite pulping process. In the context of pulp production lingosulfonates are waste products usually discharged into the enterprises’ waste waters; thus, the traditional technological process of market pulp production should be considered environmentally unsound [1].

On the other side, the sulfite pulping process can be viewed as the first stage of complex chemical processing of wood providing other branches of industry with raw materials [2, 3] and, at the same time, as a process generating additional energy for the enterprise’s own needs [4].

This article considers a possibility to use lingosulfonates in newsprint paper production [5–7]. In this case it is possible to make use of their functional properties, in particular, their surface activity. Introduction of lignosulfonates into paper-making stock as auxiliary substances makes it possible to increase the strength of the produced paper.

In case unmodified industrial lignosulfonates are used, they are held by the components of fibrous paper-making stock due to physical forces only. Therefore, it is possible that these substances will accumulate in the under-wire section of paper-making machines and, correspondingly, in waste waters. This will not reduce the environmental burden; on the contrary, it will cause additional problems.

Below we describe studies dedicated to development of various scenarios for introduction of lignosulfonates into the paper-making stock composition, ensuring their immobilization on the surface of the paper-making stock components and thus eliminating contamination of waste waters, at the same time, making it possible to produce higher quality paper.

One of the options is based on immobilization of lignosulfonates by the paper-making stock components.

To achieve strong and complete immobilization of lignosulfonates it is necessary to perform preliminary treatment of the paper-making stock, i.e. cationic polyelectrolyte is adsorbed on its surface. It is assumed that interaction of the cationic polyelectrolyte, contained by the solid surface, with anionic polyelectrolyte, represented by lignosulfonate, results in the formation of surface polyelectrolyte complexes giving new functional properties to the produced paper.

In performed research works sorption of the cationic polyelectrolyte was carried out on the solid phase components forming the composition of newsprint paper, i.e. on samples of sulfite pulp, paper-making stock, and a filler – KN84 kaolin (it can be used in the newsprint paper composition to improve ink-trapping and smoothness of the paper). Poly-*N,N*-dimethyl-*N,N*-diallylammonium chloride was used as the cationic polyelectrolyte.

The standard composition of newsprint paper included 75% of ground-wood fibers and 25% of unbleached sulfite pulp. The formation of newsprint

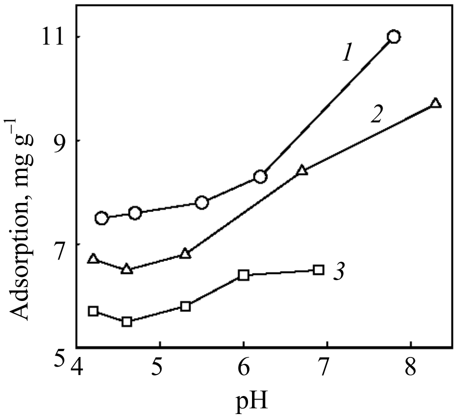

Fig. 1. Dependence of polyelectrolyte adsorption on components of paper-making stock on pH of the solution: (*1*) kaolin; (*2*) pulp; and (*3*) ground-wood.

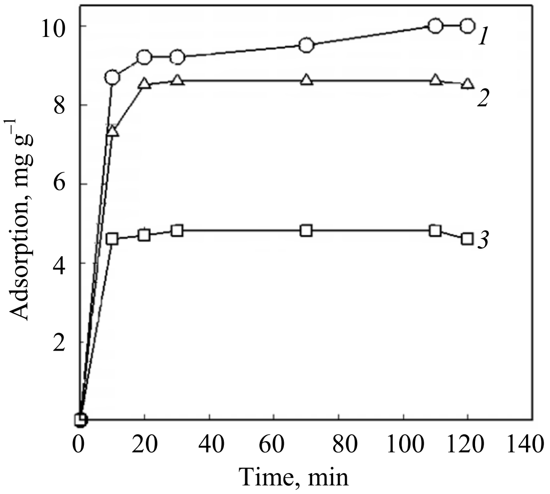

Fig. 2. Kinetic curves of cationic polyelectrolyte adsorption on components of paper-making stock: (*1*) kaolin; (*2*) pulp; and (*3*) ground-wood.

paper samples (48 g m^{-2}) was carried out at a laboratory sheet former of the Rapid-Koethen type. Physical and mechanical tests of the obtained paper samples were performed in compliance with the procedures of the GOST State Standard [8].

The influence of pH (ranging from 4 to 10) of the cationic polyelectrolyte solution on adsorption by the paper-making stock components was studied. The experimental conditions were as follows: concentration of the cationic polyelectrolyte of 250 mg dm^{-3}, hydromodule of 100, and contact period of the interacting phases of 1 h.

Adsorption of the cationic polyelectrolyte by the paper-making stock components results in acidification of the equilibrium solutions, increasing with higher pH values of the initial solutions, which points at the ion-exchange nature of the sorption process. It was determined that with increasing pH adsorption changed insignificantly within a range of 5–10 mg g^{-1} (Fig. 1), which could be related to impregnation of approximately equal active parts of the specific surface area of the sorbent samples, the paper-making stock components.

Kinetics of the cationic polyelectrolyte sorption by the paper-making stock components was studied under static conditions at concentration of the polyelectrolyte of 250 mg dm^{-3} in neutral solution at hydromodule of 100 (relation of the liquid phase to the solid) (Fig. 2). Impregnation of the solid phase with the polyelectrolyte is achieved after 30 minutes of the reagents' contact. Kaolin and sulfite pulp exhibit approximately equal level of activity in relation to the polyelectrolyte. Ground-wood is less active; its capacity in relation to the cationic polyelectrolyte does not exceed 5 mg g^{-1}, which is twice as low as the activity demonstrated by kaolin and pulp.

Isothermal curves of the cationic polyelectrolyte sorption (concentration of the chemical reagent ranging from 1 to 2000 g dm^{-3}, neutral medium, period of contact of the solid phases with the polyelectrolyte of 1 day, and hydromodule of 100) on kaolin, sulfite pulp, and ground-wood are similar in form (Fig. 3), which indicates the same mechanism of the reagent's sorption by the solid phase.

The peak value of sorption equal to 40 mg g^{-1} was observed for cellulose-containing sorbents. Kaolin (specific surface area of 10.8 m^2 g^{-1}) absorbs twice as much of the cationic polyelectrolyte; it is likely that adsorption on the aluminosilicate surface is irreversible.

The influence of hydromodule on interaction of the paper-making stock components with the cationic polyelectrolyte (concentration of the reagent of 250 mg dm^{-3}, neutral medium, and period of contact of the solid phases with the polyelectrolyte of 1 day) is shown in Fig. 4.

The form of the function of the polyelectrolyte sorption by the solid phases of different nature demonstrates that the interaction of the paper-making stock components with the polyelectrolyte is quite intensive and the formation of surface polymolecular layers of the reagent is possible.

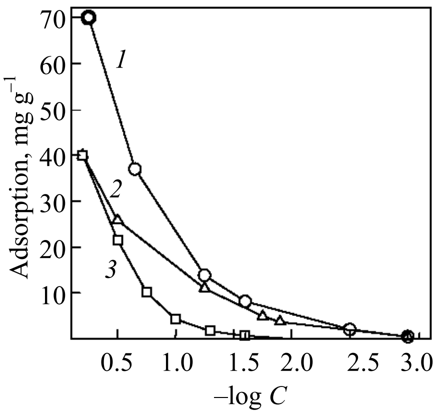

Fig. 3. Isothermal curves of cationic polyelectrolyte sorption on components of paper-making stock: (*1*) kaolin; (*2*) pulp; and (*3*) ground-wood.

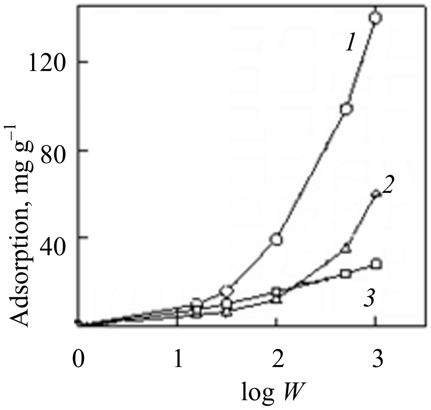

Fig. 4. Influence of hydromodule on cationic polyelectrolyte sorption by components of paper-making stock: (*1*) kaolin; (*2*) pulp; and (*3*) ground-wood.

An increase in ionic strength of the solution due to addition of NaCl results in a decrease in adsorption by 25%. When the concentration of salt ranges from 0.25–0.5 mol dm^{-3}, this value becomes constant and equals to 11.5 mg g^{-1}.

Therefore, when the surface of the paper-making stock components is treated with the cationic polyelectrolyte, it results in the formation of a polyelectrolyte layer acting as the active phase during subsequent immobilization of lignosulfonates in connection with possible formation of surface polyelectrolyte complexes.

Under conditions that are close to the process conditions for preparation of paper-making stock for newsprint paper production after the paper-making stock components are activated by the cationic polyelectrolyte, the paper-making stock is treated with lignosulfonate solution (concentration of 10 g dm^{-3}).

Ground-wood is not treated with lignosulfonates as it contains sufficient quantities of the lignin component and remains unmodified in the composition of paper-making stock.

Strength indicators of newsprint paper produced in compliance with the technology based on the composition consisting of 75% of ground-wood and 25% of unbleached sulfite pulp, modified to various degrees, are given in Table 1.

The obtained data demonstrate that modified pulp gives additional strength to the paper sheet as compared to unmodified pulp, the breaking length of which amounts to 3100 m.

When mixed compositions of sulfate pulp, i.e. unmodified and modified forms, are used, additional strengthening is observed. This effect can be related to redistribution of surface polyelectrolyte complexes throughout the pulp stock, changing its state to a more active form capable of ensuring a higher number of effective bonds with ground-wood. Thus, it is possible either to increase the ground-wood content in the newsprint paper composition, at the same time, reducing the share of expensive sulfite pulp or to introduce a filler to reduce the paper the production costs and improve the paper quality.

Table 1. Strength of newsprint paper produced using modified sulfite pulp

Pulp, % in relation to fiber		Content of lignosulfonates, % (in relation to pulp)	Breaking length, m	Whiteness, %
unmodified	modified			
10	15	0.27	3340	56
–	25	0.27	3400	56
10	15	4.40	3800	56
–	25	4.40	3550	56
10	15	8.00	3610	56
–	25	0.27	3490	56

Table 2. Increase in strength of paper, containing modified filler, with regard to breaking length (%, in relation to standard)

Consumption of cationic polyelectrolyte, mg g^{-1} of kaolin	Consumption of lignosulfonates, % in relation to kaolin				
	0.7	6.7	33	33	33
0.02	16	23	24	24	24
4.70	21	23	8.4	8.4	8.4
22.2	35	20	21	21	21

Another paper production option involves an additional operation for introduction of a filler (kaolin) containing the cationic polyelectrolyte (20 mg g^{-1}), which is repeatedly treated with the lignosulfonate solution (concentration of 10 mg dm^{-3}) at various consumption rates ranging from 0.7 to 120% in relation to the filler (content of the pulp component of the newsprint paper composition remains unchanged).

Treatment of kaolin with the cationic polyelectrolyte through adsorption gives a positive charge to the surface of the filler, thus, altering the acid-base function. Modified kaolin can absorb anion-active substances, in particular, lignosulfonates, forming surface polyelectrolyte complexes of different composition. Polyelectrolyte complexes with varying composition possess individual properties. In order to evaluate the properties of kaolin modified by way of successive treatment with the cationic polyelectrolyte and the solution of lignosulfonates, samples of the filler from the newsprint paper composition were used. In this case the newsprint paper composition consisted of 75% of ground-wood, 15% of sulfite pulp, and 10% of the modified filler.

Changes in the paper strength properties with regard to breaking length as compared to samples of the paper produced using the traditional technology are shown in Table 2. The consumption of kaolin instead of sulfite pulp amounted to 10% of absolutely dry fiber.

With changing ratios of the cationic polyelectrolyte: lignosulfonate on the surface of kaolin the paper strength changes irregularly as compared to the standard composition at variations of the ash content from 5 to 7%. This fact can stem from the specific features of polyelectrolyte complexes on the surface of kaolin, which consist of the cationic and anionic polyelectrolytes.

Therefore, application of the paper-making stock components modified with lignosulfonate gives a double practical effect – economic (resource-saving) and environmental (waste waters of the enterprise are not contaminated with lignosulfonates).

In order to diversify the production and improve the quality of paper products enterprises apply various auxiliary substances, which make it possible to regulate the paper properties and drastically decrease the paper production costs. Modified lignosulfonates can be considered such chemical additives for paper-making stock, but they are cheaper and act as fillers.

Within the framework of the problem of newsprint paper production using lignosulfonates in work [9] lignosulfonates were modified with metal ions or film-forming substances in order to increase hydrolytic stability of the system. At present, it is possible to speak about already implemented scenarios of pulp-and-paper production waste recovery with obtainment of the following products: metal derivatives containing lignin to be used as active fillers of paper-making stock [9]; micro-encapsulated lignin-containing substances to be used as fillers of paper-making stock [10]; products of copolymerization with lignin-containing substances to be used as binding materials; and modified lignosulfonates to be used for paper tinting or as pigments.

When lignosulfonates in non-aqueous medium are treated with chlorides of titanium(IV), tin(IV), or aluminum, it results in formation of the corresponding salts, which are poorly soluble in water and capable of forming dispersions. Introduction of a dispersion of modified lignosulfonates, containing 0.1–5.0% of the modifier, into the paper-making stock composition in the amount of 1–10% makes it possible to additionally increase the strength of the produced newsprint paper by 25% (breaking length of 3900 m) as compared to the reference sample [9]. In this case the dispersion of modified lignosulfonates acts as a binding and filling material simultaneously. Moreover, the paper whiteness also increases by 2% as compared to the reference sample, which is likely to be related to the stabilization of oxidation of residual lignin in the composition system of the paper-making stock.

When lignosulfonates are treated with metal chlorides in an organic solvent, adsorption of metal ions on the surface of lignosulfonates takes place, i.e. surface lignosulfonates of the corresponding metals are formed. At the same time, absence of hydrolysis in organic solvents accounts for complete formation of lignosulfonates of metals found in the solutions in the associated form.

Table 3. Physical and mechanical properties of newsprint paper produced using modified lignosulfonates

Consumption of modified lignosulfonate, % of absolutely dry fiber	Modifier		Paper properties			
	formula	quantity, % of lignosulfonate weight	weight 1 m^2	breaking length, m	bursting strength, kPa	whiteness, %
–	–	–	45.9	3100	140	56.0
0.1	$TiCl_4$	10	45.2	3720	150	57.5
5.0		1	44.8	3800	160	57.5
0.1	$AlCl_3$	10	43.3	3630	160	58.1
5.0		1	43.7	3770	160	57.0
0.1	$SnCl_4$	10	45.2	3550	150	57.0
5.0		1	45.0	3670	150	56.5

Table 4. Physical and mechanical properties of newsprint paper produced using encapsulated lignosulfonates

Consumption of lignosulfonates, % of absolutely dry fiber	Quantity of modifier, % of absolutely dry lignosulfonate	Paper properties		
		breaking length, m	bursting strength, kPa	whiteness, %
–	10	3580	160	57.9
1.0	25	3620		58.2
	10	3980		58.0
2.5	25	3960		59.1
	10	3940		58.2
20.0	25	4070		59.6
	10	4050		58.7

In case an aqueous dispersion of modified lignosulfonate is prepared, surface associates of the metal hydrolyze and form the basic salt of the metal. In the paper-making stock composition this lignosulfonate salt acts as a strengthening agent as it is capable of forming additional hydrogen bonds with fibrous semi-finished product.

Newsprint paper produced with the use of lignosulfonates modified with metal salts possesses high physical and mechanical properties (Table 3).

Application of micro-encapsulated lignin-containing substances in the newsprint paper composition (in the form of dispersions, at consumption rate of 1.5–20% of dry fiber weight) results in an increase in the paper sheet strength by 10% as compared to the reference sample (Table 4). At the same time, the paper whiteness also increases by 2–4% [10].

Chemical modification of lignosulfonates with acrylamide or epichlorohydrin with triethanolamine does not give any significant effects.

At the same time, lignosulfonates immobilized by products of polycondensation of phthalic anhydride and glycerol increase the strength of the newsprint paper to the standard level (3100 m) at the ash content of 9%, which is equivalent to savings of the semi-finished product.

When lignosulfonates in the form of gel mixed with the filler and the basic dyes are used in paper production, the paper acquires the corresponding color, its physical and mechanical properties increasing simultaneously. In this case the absorbed dye is firmly captured by the paper sheet; it acts as a pigment and does not wash out with water.

High indicators of the paper quality are ensured by application of the lignosulfonate gel at consumption rate of the reagent ranging from 0.5 to 3.5% of absolutely dry fiber. In this case the paper sheet strength almost doubles at constant ash content (~11%). Whiteness of the paper decreases insignificantly and stabilizes at a level of 70% at the indicated consumption rate of the reagents. The introduction of gelled lignosulfonates into the composition of the paper-making stock makes it possible to use calcium carbonate as a filler without changing the paper production technology developed for the process based on application of kaolin. The paper produced from such paper-making stock acquires acid-proofness.

It is principally possible to replace chrome-containing lignosulfonate gels with related systems, for example, containing aluminum hydroxide. Such systems ensure an increase in the strength of paper samples by 30% without reducing whiteness. Moreover, in such case aging of the paper slows down significantly.

Chemical modification of lignosulfonates in the epichlorohydrin–triethanolamine system at molar ratios of the reacting agents ranging from 0.5 to 3.0 makes it possible to obtain cationic lignosulfonates. In the composition of newsprint paper cationic lignosulfonates only increase the elongation parameter without changing other characteristics of the paper at consumption rate of up to 5% of the fiber weight. That means that, as demonstrated earlier, no significant effects are achieved. At the same time, in case the quantity of the modifier is increased, the paper strength additionally increases by 10%.

When the titanium form of lignosulfonates treated with hydrogen peroxide is modified with acrylamide on the basis of the radical polymerization method, the resulting products contain from 10 to 100% of acrylamide in relation to lignosulfonate. Thermochemical studies demonstrated that the modification process was accompanied by thermal effects related to the interaction of the system with water, the magnitude of the thermal effect depending on the content of acrylamide in the system. At acrylamide consumption rate ranging from 10 to 25% of lignosulfonate weight the thermal effect (ΔH) reaches 11.8 kJ kg^{-1}, which indicates acrylamide immobilization by the surface of titanium-containing lignosulfonate. Further increase in acrylamide consumption rate to 50% results in a drastic increase in ΔH to 75 kJ kg^{-1}, which explains the honeycomb structure of the surface of lignosulfonates containing polymerized acrylamide in the form of ribbon structures. At high acrylamide consumption rates (75–100%) the process of microencapsulation of lignosulfonates with the polymer takes place, ΔH value stabilizing at a level of 32–39 kJ kg^{-1}.

The results of measurements of thermal effects make it possible to explain the nature of changes in the quality parameters of newsprint paper produced using lignosulfonates modified with acrylamide. Monomeric forms of acrylamide on the surface of lignosulfonates do not lead to higher quality parameters, while polymeric forms of acrylamide in the composition of lingosulfonate stabilize these parameters, i.e. they hardly depend on the additive consumption rate at insignificant increase in strength (5–8%).

Structural changes in the surface of lignosulfonate are confirmed in case of additional introduction of sodium silicate into the composition described above (titanium complex of lignosulfonate modified with acrylamide).

Additions of sodium silicate into the system of acrylamide monomers on the surface of lingosulfonates result in stabilization of the peroxide form of the titanium complex of lignosulfonates. Sodium silicate can form a coating in the form of polysilicic acids on the surface of lignosulfonates, i.e. it causes shielding of the surface. This fact is confirmed by thermal effect values from the interaction of the system with water, ranging from 35 to 40 kJ kg^{-1}. Correspondingly, there is an increase in the strength of paper produced from paper-making stock containing 75% of ground-wood and 25% of sulfite pulp by 10–15%. At the same time, there is no deterioration in the paper sheet whiteness. The achieved results can be useful for processing of secondary fiber obtained from wastepaper materials.

REFERENCES

1. Kirsanov, V.A., Tyurin, E.T., Kirsanova, L.D., et al., *Tsellyuloza, Bumaga, Karton*, 2003, no. 10, pp. 46–48.
2. Chudakov, M.I., *Promyshlennoe ispol'zovanie lignina* (Industrial Utilization of Lignin), Moscow: Lesnaya Promyshlennost', 1983, 3rd ed., p. 200.
3. Bogomolov, B.D., Sapotnitskii, S.A., and Sokolov, O.M., *Pererabotka sul'fatnogo i sul'fitnogo shchelokov* (Processing of Sulfate and Sulfite Liquors), Moscow: Lesnaya Promyshlennost', 1989, p. 360.
4. Kirsanov, V.A. and Tyurin, E.T., *Ekologiya i Promyshlennost' Rossii*, 2006, no. 8, pp. 31–41.
5. Kurkova, E.V., *Cand. Sci. (Eng.) Dissertation*, St. Petersburg, 1992.
6. Russian Inventor's Certificate no. 1567697, *Byul. Izobret.*, no. 1, 1992.
7. Russian Inventor's Certificate no. 1567698, *Byul. Izobret.*, no. 1, 1992.
8. Dubovoi, V.K., Gur'ev, A.V., Kazakov, Ya.V., et al., *Uchebnoe posobie: laboratornyi praktikum po tekhnologii bumagi i kartona* (Handbook: Practical Laboratory Course on Paper and Board Technology), Komarov, V.I. and Smolin, A.S., Eds., St. Petersburg: Izd. Politekhn. Universiteta, 2006, p. 230.
9. Russian Inventor's Certificate no. 1776712, *Byul. Izobret.*, no. 43, 1992.
10. Russian Patent no. 2019615, *Byul. Izobret.*, no. 17, 1994.