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(54) **Titre** : METHODE POUR ATTENUER LA FORMATION D'UNE PELLICULE BIOLOGIQUE CHEZ LES PLANTES CHEZ QUI L'EAU EST RECYCLEE
(54) **Title**: METHOD FOR REDUCING SLIME FORMATION IN PLANTS HAVING A WATER CYCLE

(57) **Abrégé/Abstract**:
The invention relates to a method of reducing slime formation in plants in which water is recycled, whereby a lignosulfonate is added to the water. The lignosulfonate is produced by a special method and has a special composition, which leads to a surprisingly good effect of the added lignosulfonate.

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Abstract

The invention relates to a method of reducing slime formation in plants in which water is recycled, whereby a lignosulfonate is added to the water. The lignosulfonate is produced by a special method and has a special composition, which leads to a surprisingly good effect of the added lignosulfonate.

A method of reducing slime formation in plants having a water cycle

The present invention relates to an improved method of reducing slime formation in plants in which water is recycled, whereby a lignosulfonate is added to the recycling water.

Microorganisms often find ideal breeding conditions in the water cycles of plants. In particular the white water of paper machines, which is increasingly circulated in a closed cycle, provides ideal conditions in terms of the inorganic and organic nutrient supply, temperature, pH value and oxygen content for their unlimited breeding. This leads to a dramatically high degree of slime formation on the walls of the parts, such as the pipes, vessels and pumps, of the plant used for cycling the white water. The detachment of slimy parts from the walls leads to the formation of lumps and holes in the paper web. This weakens the paper web, i.e. breaks can occur in the paper web, resulting necessarily in machine downtime.

In the paper industry, considerable amounts of biocides are therefore traditionally added to the paper machine cycles during the production sequence to control bacterial growth. Such biocides can destroy the bacteria causing slime formation. However, due to the action and function of biocidal slime control agents they must have no fiber affinity. They therefore do not remain in the paper but leave the paper factory in the waste water. The white water contains not only the bacteria but also fungi, so that fungicides must additionally be used. The known method, also known as the "total kill" method, is therefore not only very expensive but also results in an environmental load.

In the interests of environmental protection, but also for financial reasons, it has therefore been an objective in the paper manufacturing branch to reduce slime formation in recycling water plants using environmentally acceptable but nevertheless effective means.

U.S.-A-2,551,446 describes the use of a cuprous salt, e.g. copper sulfate, to prevent the growth of microorganisms in water. To prevent the copper sulfate from precipitating one uses a lignosulfonate as a complexing agent. CA-A-807,123 discloses the use of halogenated levulinic acid as a biocide. Since halogenated levulinic acid is only slightly soluble in water, lignosulfonic acid and dimethyl sulfoxide are proposed as dispersing agents.

It is known from "Das österreichische Papier" 20, no. 9, 34-35, to add a lignosulfonate together with a biocide to the white water of a paper machine. This makes it possible to reduce the amount of biocide added.

It is assumed that the lignosulfonate neutralizes by electrostatic charge equalization the metabolic products acting as a food bridge to the cycling system, thereby making them useless for the food supply. This controls the bacterial activity and thus also the fungal attack. The mentioned article states that a "specially selected and modified lignosulfonate" is used as a biological complexing agent. It is not mentioned which "specially selected and modified lignosulfonate" this is. Commercial lignosulfonates are in any case unsuitable for the stated purpose, as experiments have shown.

European patent no. 0 185 963, which is from the same applicant, discloses a method of reducing slime formation in water cycles using a lignosulfonate having a weight-average molecular weight of 4000 to 7000 (number average 2000 to

3000). This method achieves good results in reducing slime formation.

However, operation has shown that the known special lignosulfonate does not fully meet the requirements. It fails when the flow is reduced or fully lacking in the water cycle, for example in certain areas of the plant.

The present invention is based on the problem of overcoming this disadvantage, in particular of providing a lignosulfonate product having improved properties for preventing slime formation.

It was assumed that the efficacy of the known lignosulfonate is based on its low viscosity and thus its low molecular weight. On this assumption lignosulfonates were produced by fractionation so as to have an even lower molecular weight. However, these lignosulfonates showed little or no improvement.

Surprisingly enough, an abrupt improvement in the reduction of slime formation occurs if a lignosulfonate is used which is produced by mixing a calcium-impoverished sulfite lye of an acidic wood sulfite pulp with an amount of calcium hydroxide which suffices to deposit calcium lignosulfonate with a higher molecular weight, and treating the remaining soluble part with sodium sulfate and sulfuric acid to separate the calcium largely in the form of calcium sulfate out of the sulfite lye which contains the lignosulfonate, and optionally concentrating the sulfite lye containing the lignosulfonate.

The use of this lignosulfonate leads to a considerable improvement in the break data during operation of a paper machine. One reason for this is presumably that the lignosulfonate shows an elevated effect even when there is less or no flow in the water recycling. When the fouling situation in the paper machine cycle is quantitatively reduced and qualitatively improved, this obviously reduces the machine's susceptibility to disturbance with respect to breaks, lumps or holes in the paper web due to fouling.

The weight-average molecular weight of the inventively used lignosulfonate is preferably 8000 to 15000; the number-average molecular weight is 1000 to 3000.

The molecular weight of the inventively added lignosulfonate is preferably about 12700 on the weight average and about 1564 on the number average. In a further preferred embodiment the molecular weight of the added lignosulfonate is 8500 on the weight average and 1500 on the number average. With these lignosulfonates one obtains particularly good and stable results.

Surprisingly enough, a lignosulfonate product having a higher molecular weight than the known lignosulfonate product thus leads to an improvement in the reduction of slime formation. It is assumed that this is mainly due to the content of oligosaccharides of 12 to 16 weight percent.

Further characteristics of the inventively used lignosulfonate are that it is obtained from a wood consisting at least partly of softwood, whereby this product has a low content of reducing sugars of at most 1.0 weight percent. It is known that reducing sugars support the growth of microorganisms. The degree of sulfonation of the lignosulfonate product is preferably 1.2 to 1.5.

A further feature of the inventively used lignosulfonate product is that it contains a quantitative share of 40-55% short-chain (1-5 pentose and/or hexose units) of partly oxidatively altered fragments of cellulose and cellulose accompanying substances.

The lignosulfonate can be used in the inventive method in a concentration of 0.1 g to 1.0 g/m^3 water. The lignosulfonate is charged continuously. To further reduce any lump formation one can also add to the recycling water small amounts of the biocides known for this purpose. The biocide is added periodically, the time during which biocide is added being 4 to 50% the time during which lignosulfonate is added.

The biocides used may be one or more organic sulfur-nitrogen compounds or organic bromine-nitrogen compounds, e.g. methylene-bis-thiocyanate or carbamates or 2,2-dibromo-2-cyanoacetamide or 3,5-dimethyl-1,3,5-2H-tetrahydrothiadiazine-2-thion.

The advantageousness of the inventive method shall be shown in the following with reference to comparative experiments. For this purpose, the lignosulfonate known from European patent no. 0 185 963 (product A), a commercial product (product X) and the inventively used product (product B) will be contrasted.

The inventively used, repeatedly fractionated and modified product is produced as follows.

Wood chips are subjected to the customary conditions of sulfite pulping.

44 parts by weight of calcium hydroxide ($Ca(OH)_2$) are added to 272 parts by weight of the sulfite lye of the acidic wood sulfite pulp, which is poor in calcium and contains 45% solids. The separated calcium lignosulfonate with a higher molecular weight is removed by filtration. 22 parts by weight

of 36% sulfuric acid (H_2SO_4) are added to the filtrate per 130 parts by weight of solids. The separated calcium sulfate is removed by filtration and the filtrate is concentrated by evaporation to 40% solids content. To 102 parts by weight of this, 16 parts by weight of sodium sulfate (Na_2SO_4) and 2.3 parts by weight of sulfuric acid (H_2SO_4) are added. The calcium sulfate deposit is removed by filtration and sodium hydroxide is added to the filtrate to set the pH to 7.5. One thereby obtains 100 parts by weight of solids of the product, and the solution can optionally be concentrated further.

The obtained product has the following composition in %:

Total S	6.3
Unsulfon. S	0.9
Sulfon. S	5.4
Na	11.0
Ca	0.6
Phenolic OH	1.2
OCH_3	5.6
Sugar	0.5
Na lignosulfonate	43

The resulting product has a weight-average molecular weight of about 12700 or a number average of about 1570. Obviously, other molecular weights within the claimed range can be obtained by slightly varying the described method. The content of oligosaccharides in the obtained product is about 14 weight percent.

Experiment 1

In a paper machine (300 TATO Production Wood-free/Coated) lignosulfonate products A, B and X were each used for a period of three months. The average number of breaks in the paper webs, which is a criterion for slime and fouling control in paper machine cycles, was determined. Product parameters and results are shown in Table 1.

The Table indicates that an improvement in the break number can be obtained with a lignosulfonate product according to the present invention. In comparison to a lignosulfonate according to European patent no. 0 185 963 the improvement is 10%; in comparison to commercial lignosulfonates it is even 20%.

Experiment 2

Cultures of slime-forming bacteria, for example Pseudomonas fluorescens, were each mixed with solutions of lignosulfonate A, B and X. Capillary flow time measurement (glass capillaries, liquid volume sent through and pressure conditions are constant) was used to determine time-dependent changes in viscosity. Simultaneously a blank test, i.e. with no addition of lignosulfonate, was made. The nutrient broths were stirred for a period of 24 hours and thereafter the agitator was switched off. The result is shown in Table 2.

As indicated in Table 2, viscosity increases considerably during an operating time of 100 hours when no lignosulfonate is added. By contrast, lignosulfonates A and B substantially prevent an increase in viscosity.

An interruption of the circulation causes a pronounced increase in the viscosity of the cultures that are mixed with lignosulfonate A or contain no additive. The culture with lignosulfonate B added shows virtually no increase in viscosity. Thus, while lignosulfonates A and B can prevent the formation of bacterial slime in moving systems, such as the piping and troughs carrying pulp or white water in a paper machine, the inventively used lignosulfonate B provides the essential additional effect of reducing slime formation even in nonmoving systems. This is of crucial importance for those critical zones in a paper machine cycling system which are characterized by a highly reduced or fully lacking flow. Slime formation generally occurs first and to a greater degree in such places.

Obviously, this effect provided by the inventively used lignosulfonate is of crucial importance for the method. It can substantially improve the break number.

An improved break number simultaneously improves the economy of the method, since less unwanted machine down-time is required.

Table 1

	MW	Degree of sulfonation (%)	Oligosaccharides (%)	Ø Breaks/ 100 tons
A	4000-7000	1.2 - 1.5	25 - 40	2.75
B	12700	1.2 - 1.5	12 - 16	2.5
X	±50.000	0.7	undefined	3.2

Table 2

Increase in viscosity (η)

Product	Starting value	After 100 h with circulation	After 100 h more w/o circulation
A	1	1.1	3.1
B	1	1.1	1.3
W/o additive	1	1.7	3.4

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of reducing slime formation in plants in which water is recycled, whereby a lignosulfonate is added to the water, **characterized** in that the lignosulfonate is produced by mixing a calcium-impoverished sulfite lye of an acidic wood sulfite pulp with an amount of calcium hydroxide which suffices to deposit calcium lignosulfonate with a higher molecular weight, and treating the remaining soluble part with sodium sulfate and sulfuric acid to separate the calcium largely in the form of calcium sulfate out of the sulfite lye which contains the lignosulfonate, and optionally concentrating the sulfite lye containing the lignosulfonate.

2. The method of claim 1, **characterized** in that the lignosulfonate has a weight-average molecular weight of 8000 to 15000 or a number-average molecular weight of 1000 to 3000.

3. The method of claim 1, **characterized** in that the lignosulfonate has a weight-average molecular weight of 12700 or a number-average molecular weight of 1564.

4. The method of claim 1 and/or 2, **characterized** in that the lignosulfonate has a weight-average molecular weight of 8500 or a number-average molecular weight of 1500.

5. The method of at least one or more of the above claims, **characterized** in that the lignosulfonate product contains 40-55% short-chain, partly oxidatively altered fragments of cellulose and accompanying substances thereof.

6. The method of claim 5, **characterized** in that the lignosulfonate has a share of oligosaccharides of 12 to 16 wt%.

7. The method of at least one of claims 1 to 6, **characterized** in that the lignosulfonate has a share of reducing sugars of at most 1 wt%.

8. The method of one or more of the above claims, **characterized** in that the lignosulfonate has a degree of sulfonation of 1.2 to 1.5.

9. The method of one or more of the above claims, **characterized** in that the lignosulfonate is added in an amount of 0.1 to 1.0 g/m^3 water.

10. The method of one or more of the above claims, **characterized** in that the lignosulfonate is obtained from a wood consisting at least partly of softwood.

11. The method of one or more of the above claims, **characterized** in that a biocide is added additionally.

12. The method of claim 11, **characterized** in that the biocide is used in an amount of 0.01 to 2.0 g/t water.

13. The application of the method of one of the above claims for reducing slime formation in a plant that recycles the white water of paper machines.