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## SLIME CONTROL

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This invention relates to slime control agents and to a method of controlling slime in pulp and paper mill systems, particularly where unbleached sulfate or kraft pulp is present.

The aqueous suspensions of fibers of the pulp and paper industry are excellent culture media for both the bacterial and fungous types of microorganisms which produce troublesome organic growths. These growths, known as slimes, vary from rubbery gums to soft gelatinous masses, and form on the inner surfaces of storage chests, pipes, and other equipment. From time to time, clots or sheets of slime break loose causing "slime spots" in the sheet of paper formed from the pulp suspension, with serious detrimental effects either as breaks in the web of paper or as unsightly defects which lower the quality of the paper. The slime growths also cause clogging of screens, pipes, etc., necessitating shut-downs of equipment for clean-up.

A number of chemical agents have been used for controlling slime in papermaking processes, with varying degrees of success. Of these, the usual organic mercurial compounds have, in many respects, proved the most satisfactory because of their high disinfectant properties. However, it has been observed that when these agents are used with unbleached sulfate or kraft pulp, their efficiency is severely reduced. This decrease in efficiency in controlling slime is rather unexpected since a corresponding treatment of sulfite pulp, soda pulp, or ground-wood with organic mercurials gives good results.

I have discovered that the cause for the relatively poor behavior of organic mercurials in controlling slime in unbleached sulfate systems has been associated with the fact that those commonly used for this purpose have proved to be more or less deteriorated or impaired by the presence of sulfide ions.

I have found that mercurated benzene sulfonic acid when used in unbleached sulfate pulp systems effectively controls slime, particularly when added in the form of a salt, as for example, sodium m-hydroxymercuribenzene sulfonate. The sodium salt has a higher solubility and appears to work better than the free acid.

The combination of properties possessed by these compounds uniquely fills a need in the pulp and paper industry. They are sufficiently soluble to be immediately effective against microorganisms, not only in ordinary pulp and paper

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mill systems but also in the case of modern, rapidly operating, kraft papermaking machines. In contrast, organic mercurials previously employed in slime control usually have a low solubility and low rate of solution and as a result are able to exert only a portion of their bactericidal action or are carried out of the system before being effective. Furthermore, the slime control agents of this invention, being compounds of a relatively strong acid, do not hydrolyze readily and are stable under both alkaline and acid conditions.

However, of more importance is the high stability of these agents toward the sulfide ion; the compounds have the high bactericidal and fungicidal properties typical of the better organic mercurial slime control agents and retain these properties in the presence of sulfide-ion—containing pulp while other organic mercurials do not.

By the term "high sulfide ion stability" it is meant that the organic mercurial is not precipitated, decomposed, blocked, or otherwise impaired to substantially reduce its slime inhibiting properties by the presence of sulfide ions.

The sulfide ion stability may be determined by a simple procedure which consists in adding a definite amount of sodium sulfide solution to a solution of organic mercury compound, then adding a slight excess of acetic acid and noting the time of appearance of a black precipitate of mercuric sulfide. The rate of decomposition of organic mercury compounds by sulfide ion can also be calculated from electrophotometer readings. Mercurated benzene sulfonic acid and its soluble salts have been found by this test to be highly stable toward sulfide ion and in actual practice to be effective as a slime controlling agent in unbleached sulfate pulp systems.

The following table shows a comparison between the rate of decomposition of No. 1, phenylmercuric borate, a typical organic mercurial slime control agent, and No. 2, mercurated benzene sulfonic acid. Mercury sulfide is precipitated so rapidly from phenylmercuric solutions that electrophotometer readings could not be made while mercurated benzene sulfonic acid was only slightly decomposed in 16 hours and shows little further change after continued contact with sulfide ion. At temperatures lower than 50° C. mercurated benzene sulfonic acid compounds showed no appreciable decomposition.

*Rate of decomposition by sulfide ion*

| Time in Minutes | 50° C. | | | | 70° C. | | | |
|---|---|---|---|---|---|---|---|---|
| | pH 3.5 | | pH 8.5 | | pH 3.5 | | pH 8.5 | |
| | No. 1 | No. 2 | No. 1 | No. 2 | No. 1 | No. 2 | No. 1 | No. 2 |
| | | Per cent | | Per cent | | Per cent | | Percent |
| 15 | Gray | | Gray | | | | Black | |
| 30 | Black | | Black | | Black | | | |
| 60 | | 1.77 | | 2.42 | Complete. | 3.54 | Complete. | 5.12 |
| 240 | Complete. | | Complete. | | | | | |
| 960 | | 3.55 | | 4.34 | | 26.65 | | 18.41 |

I have found if no black precipitate is formed in the presence of sulfide ion within 60 minutes at 50° C. the organic mercurial will have a suitable sulfide ion stability for use in sulfate mills.

One manner of carrying out my invention is as follows: sodium hydroxymercuribenzene sulfonate in powdered form is added to a pulp slurry made up in total or in part of unbleached sulfate pulp at the beater in the ratio of one ounce of active organic mercurial to about three tons of dry weight of pulp. A convenient manner of addition at the beater is in the form of paper envelopes of the powdered salt which are disintegrable under the beater roll. Where no beater is used and the system is a closed one, the powder is thrown into the white water at a point of turbulence. Any point where thorough mixing of the agent with the pulp is obtained is suitable. Paper formed from the thus treated furnish is substantially free of slime spots and the paper machine system does not suffer from clogging of screens, etc., due to slime.

The acid form of mercurated benzene sulfonic acid is effective as a germicide in unbleached kraft systems, but being very hygroscopic and relatively acidic it cannot be packaged in paper.

Other water-soluble salts of mercurated benzenesulfonic acids such as those of potassium, calcium, magnesium, and barium, are also suitable. The sodium salt has a high solubility, in the range of 150 grams per liter. The alkaline earth salts are of lower solubility; the calcium salt is soluble to the extent of 28.4 grams per liter, the magnesium 22.8 grams per liter, and the barium 18 grams per liter. The free acid is less soluble than the salts but has a high solubility in the presence of acids such as sulfuric acid. In comparison the common organic mercurial slime control agents are only slightly soluble.

The preparation of mercurated benzene sulfonic acid may be carried on as follows: commercial benzene sulfonic acid is mixed with a 50% acetic acid solution and powdered yellow mercuric oxide is added slowly at a temperature of 100° C.; the heating is continued until the precipitate of mercuric benzenesulfonate is rearranged to the soluble mercurated product. The proportions used are such that chemical equivalents of acetic acid and mercuric oxide are present while the benzene sulfonic acid is present in 10% excess on the mercuric oxide. After the reaction product has been cooled to room temperature sufficient solid sodium hydroxide is added carefully, while the system is stirred and cooled, to form the sodium salt of hydroxymercuribenzene sulfonic acid. The material is dried, then ball milled and packaged in envelopes. Other salts are prepared by neutralizing the acid with the appropriate base.

While the slime control agents of this invention are particularly adapted for use with unbleached sulfate pulp, they are effective as well with bleached sulfate and other types of pulp. They are applicable in general as disinfectants.

The term "unbleached sulfate pulp" as used in this specification and appended claims covers unbleached wood pulp produced by the sulfate pulping process and any modification thereof wherein the pulping liquor employed contains sulfide ion.

While the invention has been described with particular reference to sodium m-hydroxymercuribenzene sulfonic acid, other isomers and other analogous aromatic compounds, advantageously mono-mercurated, and which have a high sulfide-ion stability and are readily soluble in water, are included within the scope of the invention.

I claim:

1. A process of controlling slime in pulp and paper mill systems containing unbleached sulfate pulp which comprises adding a compound from the group consisting of mercurated benzene sulfonic acid and its soluble salts to an aqueous suspension of unbleached sulfate pulp in an amount sufficient to control slime.

2. The process of controlling slime in pulp and paper mill systems containing sulfide-ions which comprises adding thereto the sodium salt of mercurated benzene sulfonic acid in an amount sufficient to control slime.

3. Process which comprises adding a compound from the group consisting of mercurated benzene sulfonic acid and its water-soluble salts to an aqueous suspension of wood pulp containing sulfide-ions in an amount sufficient to control slime.

4. A process of controlling slime in pulp and paper making systems containing unbleached sulfate pulp which comprises adding to an aqueous suspension containing unbleached sulfate pulp the sodium salt of mercurated benzene sulfonic acid in the amount of about one ounce per six thousand pounds of dry pulp.

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