I have discovered that by utilizing xylene sulfonic acid-formaldehyde condensates and salts thereof as pitch dispersants in paper making and particularly in the "sulfate" method of pulping, the amount of pitch dispersed during the normal paper making process is quantitatively superior to the amount dispersed by any of the known pitch dispersants particularly the naphthalene-sulfonic acid-formaldehyde condensates and their salts. Another advantage achieved by utilizing the pitch dispersants of this invention in a paper making process is that the amount of pitch accumulated on the wires of a paper machine or on parts of machines used in the paper making process is substantially reduced when compared with the amount which accumulates when using the known dispersing agents such as the naphthalene sulfonic acid-formaldehyde condensates and their salts. This results in a marked reduction in the shut down time in the paper making operation and a decided improvement in screening conditions and pulp cleanliness as well as an improved quality pulp.

As indicated above, the greatest importance of the new method lies in the possibility of eliminating the difficulties caused by pitch in the production of paper, above all in the operation of the paper machines. For most purposes, the xylene-sulfonic acid-formaldehyde condensate should be added to the paper making process in amounts of from 0.05% to about 5.0% based on the weight of the dry pulp added to effectively reduce the amount of troublesome pitch during a paper making operation. The xylene-sulfonic acid-formaldehyde condensates may be added in greater amounts than 5.0% without detracting from any of their beneficial properties as pitch dispersants. Since no additional beneficial results in the pitch dispersing properties were noticed in concentrations of above 5%, it would seem to be impractical and uneconomical to utilize larger amounts. The xylene-sulfonic acid-formaldehyde condensates may be added to the system in the form of a dry powder, or as a water solution.

The preferred pitch dispersant for use in the process of paper making is the sodium salt of xylene-sulfonic acid-formaldehyde condensate. Other salts may be used in this process such as the potassium, calcium, lithium, magnesium, zinc as well as any of the other known salts of sulfonic acid.

Generally the pitch control agent is added to the pulp prior to the screening or refining operation so that it may be mixed with the pulp for a period of from about 30 to about 60 minutes to obtain the maximum dispersing effect. The efficacy of the pitch dispersants of the present invention was completely demonstrated on a full plant scale in several successive pulping and paper making operations. First, a 7½% water solution of the sodium salt of xylene sulfonic acid-formaldehyde condensate was fed into groundwood pulp at the rate of six pounds per ton of dry pulp. The introduction of the pitch dispersant into the groundwood pulp was made at the kneader and prior to the mechanical pulping operation. Data obtained from mill records established that during test periods of six days after continued use of the novel pitch dispersant of this invention, that when the groundwood deckers were cleaned after every six hour period, there was no build up of pitch on the groundwood deckers. In addition there was no build up of pitch on the Fourdriner wires during the test period. On the other hand, mill tests utilizing naphthalene sulfonic acid-formaldehyde condensates at the same rate instead of the pitch dispersant of this invention showed that the amount of pitch dispersed on Fourdriner wires of the machine and at the groundwood deckers was considerably greater. This is attributable to the markedly improved pitch dispersing properties of the xylene sulfonic acid-formaldehyde condensates which produced markedly improved screening conditions. In addition, an improved quality pulp was produced by utilizing the pitch
dispersant of this invention in the above process. Furthermore, although the actual consumption of chlorine in the bleaching operations carried out in the above operation had not been noticeably reduced, there was a noticeable increase in the brightness of the pulp when compared with equivalent amounts of bleaching agent used in connection with a naphthalene sulfonic acid condensate. As a result of better screening conditions in the above mill test utilizing the sodium salt of the xylene-sulfonic acid-formaldehyde condensate, the pulp was cleaner and tailings and rejects were lowered.

In a paper mill which produces light weight, heavily refined papers, utilizing predominately a high resin content sulfate pulp as its basic fiber, pitch accumulating on the refining equipment, the Fourdrinier wires and the walls has proven particularly troublesome. It has been found that utilizing various pitch dispersing agents such as the naphthalene sulfonic acid-formaldehyde condensate type resins, gave good pitch control but that not less than 20 lbs. of this dispersant per ton of dry pulp was needed to give satisfactory pitch dispersion. It was shown in an extended mill evaluation that the material of this invention controlled the pitch adequately at one-half the above rate. At this rate of application, no pitch appeared on the paper machine parts or on the beating and refining equipment. Cutting back the rate of naphthalene sulfonic acid-formaldehyde condensate caused pitch to build up at these points.

The improved dispersing action provided by the xylene sulfonic acid-formaldehyde condensate makes it useful as a dispersing agent in recovering tall oil by the method disclosed by Säller in U.S. Patent 2,802,845, from the sulphate soap skimmings produced in the paper making process. It has been found by utilizing the xylene sulfonic acid-formaldehyde condensates in the separation of tall oil from spent acid and lignin, higher yields and greater purity of tall oil were obtained than by using naphthalene sulfonic acid-formaldehyde condensates. The xylene sulfonic acid formaldehyde also provided improved retardation of the agglomeration of lignin, thus reducing time consuming clean-up periods.

The utilization of the dispersing agents of this invention in pulp slurries and tall oil soap solutions should be such that the addition is made prior to the point where the dispersing action is needed and with sufficient retention time (in 30 minutes to 1 hour or longer) so that the dispersing agent is completely admixed with the slurry for optimum effects. This can be accomplished in the pulping process by adding the agent so that it is mixed in the stock chest or other mixing points in the system prior to the screening operation. In paper making systems the addition is best made on the wet end system prior to the beating and refining operations. In the tall oil recovery system disclosed by Säller in U.S. Patent 2,802,845 the addition point should be prior to the centrifuging operation.

The xylene sulfonic acid-formaldehyde condensates and their salts may be used in xylene sulfonation of xylene with excess sulfuric acid and thereafter condensing the resulting xylene sulfonic acid with formaldehyde. The condensate may then be neutralized with a base, e.g., sodium hydroxide and the product, if desired, may then be treated to remove or reduce the water content, for instance, by spray drying.

The formation of the desired xylene sulfonic acid which can later be utilized by condensing with formaldehyde to produce the pitch dispersant of the invention is accomplished by heating at elevated temperatures at least one mole of sulfonic acid per mole of xylene so as to produce the desired sulfonation. Generally it is impractical to utilize above 5 moles of sulphuric acid per mole of xylene since the unreacted sulfuric acid may dilute the effectiveness of the final product. Sulfonation may be carried out in the presence of an inert organic solvent such as VM&P naphtha. In this manner, water formed during sulfonation may be removed by azeotropic distillation. For best results sulfonation should be carried out at temperatures of 95°C and below 150°C. Temperatures above 150°C may be utilized, but generally it is impractical and uneconomical to use such high temperatures. Any conventional procedure for sulfonating xylene may be utilized to produce xylene sulfonic acid.

In the condensation of xylene sulfonic acid and formaldehyde, temperatures of from about 75°C to 115°C, and reaction times of about 30 minutes to 20 hours or more may be utilized. In this reaction, formaldehyde, paraformaldehyde, trioxane or any material liberating formaldehyde may be used. As a matter of convenience, a 27% by weight alcohol solution of formaldehyde may be used, since it is available commercially. The amount of formaldehyde utilized in the condensation reaction may vary from 0.2 to 1.5 moles of formaldehyde per mole of xylene sulfonic acid.

The neutralization of the condensate may be accomplished by introducing either as a solid or as an aqueous solution, a neutralizing agent. Any base or basic salt which forms a sulfonic acid salt may be used as a neutralizing agent. The base may be added together with the condensate in the sulphite mill or paper mill so as to form the salt directly in the mill. Alternatively, it may be convenient to form the salt by adding the base directly to the condensate before addition to the paper mill or sulphite mill. Typical neutralizing agents include sodium hydroxide, potassium hydroxide, calcium hydroxide, barium hydroxide, as well as zinc, lithium and magnesium hydroxides.

The amount of neutralizing agent should preferably be approximately the stoichiometric amount required to neutralize the sulfonic acid condensate as well as unreacted sulfuric acid since a large excess thereof will result in an impure product. The neutralizing agent may also be supplied in a stoichiometric deficiency. The neutralized product may be utilized in the paper mill in the form of an aqueous solution or the amount of water may be reduced or the water may be removed entirely by spray drum or tray drying.

The following examples illustrate the present invention, however, they are not to be construed in a limiting sense.

**EXAMPLE I**

212 grams of xylene (2 moles) were placed in a flask. Then 294 grams of concentrated sulfuric acid (3 moles) was slowly added to the flask and the temperature rose to 80°C. After all of the sulfuric acid was added, the temperature was held at 80°C to 85°C for one hour. After this period 75 grams of water and 110 grams of 37% formaldehyde (1.35 moles) were added under constant stirring to the flask and the temperature rose in the flask to about 90°C. When all of the water and formaldehyde were added the temperature of the flask was maintained at 110°C for five hours. After this period, there was no noticeable smell of formaldehyde and the flask was cooled to room temperature. Next 320 grams of 50% aqueous sodium hydroxide solution (4 moles) and 100 grams of water were added to the flask so as to produce the sodium salt of xylene sulfonic acid-formaldehyde condensate which was a dark red viscous liquid. This product was then spray dried to remove the water.

**EXAMPLE II**

106 grams of xylene (1 mole) was placed in a flask. Then 245 grams of concentrated sulfuric acid (2.25 moles) was added slowly to the flask and the temperature rose to about 50°C. During the addition, the flask was cooled so as to maintain a temperature of 50°C. After all of the sulfuric acid was added, the temperature was held at 50°C for 20 minutes. After this period 75 grams of water and 82 grams of a 37% formaldehyde solution were slowly added under constant stirring to
the flask and the temperature rose in the flask to about 80° C. When all of the water and formaldehyde were added, the temperature of the flask was maintained at 80° C. for two hours. After this period, it was observed that there was no noticeable smell of formaldehyde and the flask was cooled to room temperature. Then 200 grams of an aqueous 50% sodium hydroxide solution (2½ moles) and 100 grams of water were added to the flask so as to produce the sodium salt of xylene sulfonic acid-formaldehyde condensate which was a dark red viscous liquid. This product was then dried at room temperature for two days to remove the water.

EXAMPLE III

In this example, the prior art dispersant, viz., the condensate of naphthalene sulfonic acid-formaldehyde was prepared utilizing the proportions of Example I above. 256 grams of naphthalene (2 moles) was placed in a flask. Then 294 grams of concentrated sulfuric acid (3 moles) was slowly added to the flask and the temperature rose to 80° C. After all of the sulfuric acid was added, the temperature was held at 80 to 85° C. for one hour. After this period, 75 grams of water and 110 grams of 37% formaldehyde (1.35 moles) were added under constant stirring to the flask and the temperature rose in the flask to about 90° C. When all of the water and formaldehyde were added, the temperature of the flask was maintained at 110° C. for five hours. After this period, there was no noticeable smell of formaldehyde and the flask was cooled to room temperature. Next 320 grams of 50% aqueous sodium hydroxide solution (4 moles) and 100 grams of water were added to the flask so as to produce the sodium salt of naphthalene sulfonic acid-formaldehyde condensate which was a dark red viscous liquid. This product was then spray dried to remove the water.

EXAMPLE IV

The following test was performed to determine the relative pitch dispersing properties of the compounds prepared by Examples I, II and III. 15 grams of shredded alpha cellulose pulp (produced by the soda pulping process) was placed in a tank containing 500 cc. of water. 15 grams of pitch, which in this case was the sap from the Balsam Fir tree, was also added to the tank. Separate runs were made, each using 0.15 gram of one of the dispersants prepared in Examples I, II and III. In each of the runs, the mixture was agitated at 180° F. by a mechanical agitator for 2 hours which was weighed before use. After agitation was finished, the agitator was removed and dried in an oven at 100° C. for 30 minutes and the increase in weight determined. This represented the amount of un-dispersed pitch which collected on the agitator. A blank run was made wherein no dispersant was used. The percent pitch for each run including the blank was calculated as

\[
\text{Percent pitch} = \frac{\text{Increase in weight of agitator}}{\text{Weight of known pitch added} \times 100}
\]

The results for each determination are tabulated below.

<table>
<thead>
<tr>
<th>Dispersant used:</th>
<th>Percent pitch</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (blank)</td>
<td>44.6</td>
</tr>
<tr>
<td>Example III (prior art)</td>
<td>28.9</td>
</tr>
<tr>
<td>Example II</td>
<td>18.9</td>
</tr>
<tr>
<td>Example I</td>
<td>15.2</td>
</tr>
</tbody>
</table>

As seen from the above table, utilizing xylene sulfonic acid-formaldehyde condensate in place of naphthalene sulfonic acid-formaldehyde condensate reduces the amount of pitch deposited on the agitator by almost half. Hence it is seen that xylene sulfonic acid-formaldehyde condensate is a superior pitch dispersing agent than known pitch dispersing agents such as naphthalene sulfonic acid-formaldehyde condensate.

My dispersants can also be utilized with the same beneficial results with either bleached or unbleached pulp produced from the groundwood (mechanical pulping), semi chemical, chemi-groundwood, sulfate, sulfite (kraft), or cold soda pulping processes. My dispersants may be utilized to disperse pitch in the making of pulp as well as in the subsequent paper making steps. However, it is understood that my invention is not limited to any specific process of making pulp or paper but is useful wherever the problem of pitch arises in paper making and pulping.

Having described my invention what I claim is new

and desire to secure by Letters Patent is:

1. In pulp and paper making processes, a method of preventing deposition of pitch from pulp which comprises adding to the pulp a material selected from the group consisting of xylene sulfonic acid-formaldehyde condensates and their basic salts in the amount of from about 0.05% to about 5% calculated on the weight of dry pulp.

2. In pulp and paper making processes, a method of preventing deposition of pitch from pulp which comprises adding to the pulp the sodium salt of xylene sulfonic acid-formaldehyde condensate, said salt being added in an amount of from about 0.05% to about 5%, calculated on the weight of dry pulp.

3. In the pulping of wood, the improvement which comprises adding to the pulp a material selected from the group consisting of xylene sulfonic acid-formaldehyde condensate and its basic salts and thereafter screening said pulp, said screening taking place at least 30 minutes after said material is added to the pulp, said salt being added in an amount of from about 0.05% to about 5%, calculated on the weight of the dry pulp.

4. The process of claim 3 wherein said material is the sodium salt of xylene sulfonic acid-formaldehyde condensate.

5. In pulp and paper making processes, a method of preventing deposition of pitch from alpha cellulose pulp comprising the step of adding to alpha cellulose pulp, a material selected from the group consisting of xylene sulfonic acid-formaldehyde condensates and their basic salts in an amount of from about 0.05% to about 5%, calculated on the weight of dry pulp.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION
Patent No. 3,154,466

October 27, 1964

William M. Nothum

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 69, for "sulfonic" read -- sulfuric --.

Signed and sealed this 8th day of March 1966.

SEAL:
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents
UNITED STATES PATENT OFFICE
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