Pitch deposition in papermaking and the function of pitch-control agents

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ABSTRACT *Dispersed synthetic pitch was deposited by inducing shearing forces. The deposition tendency of two types of pitch was evaluated with regard to the influence of temperature, water hardness, pH, concentration, and fiber consistency. The effect of pitch-control agents (alum, talc, and three polymers) on the extent of deposit formation was then studied. The conditions required for deposition and the extent of deposit formation were dependent on the composition of the dispersed pitch. Certain pitch-control agents profoundly reduced pitch deposition, with Darasperse® cationic polymers being the most effective. A mechanism by which such polymers work is suggested.*

KEYWORDS
Pitch control
Cationic compounds
Synthetic polymers
Aluminum potassium sulfate
Talc
Kraft pulping
Neutral sulfite pulping

The formation of deposits of resinous substances (pitch, stickies) in paper machine systems presents a serious problem for the paper industry and has been the subject of many papers published over several decades. Despite considerable effort, it has not been possible to clearly elucidate the mechanisms of deposit formation because of the extreme complexity of these systems. Reasonable guesses and suggestions have been made over the years, and these have recently been summarized in the literature (*1*). Few parameters governing the rate and extent of deposit formation are known.

Allen (*2*) has found that the concentration of pitch particles is one important parameter. Several authors (*3–6*) have suggested that resin viscosity is important, but none have provided any strong evidence supporting this suggestion. Back (*3*) notes that pitch deposition is influenced by the nature of the metal surface upon which it is deposited. He has found a correlation between deposit formation and the rate of soap formation in water suspensions for various metals.

It is further known that many factors may greatly influence the tendency of a pulp to form deposits. Included among these factors are pulpwood handling and storage time (*7–10*), composition of the mill water supply (*11–13*), and the pulping procedure (*14, 15*). The reasons why these factors influence the tendency for deposition are, however, generally not known.

Pitch-control agents

The paper industry has been using deposit-control agents for many years to avoid the problems caused by pitch deposition. Alum, talc, and anionic pitch-control agents, such as polynapthalene sulfonates or modified lignosulfonates, have been the dominant materials used for this purpose.

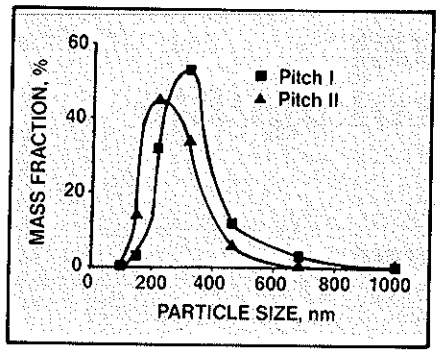
There has been a considerable effort to characterize the chemical nature of pitch and the causes of deposition. However, the effects of pitch-control agents have not received much attention. The few papers that have been published deal only with alum (*16*) or talc (*17–19*). The mechanisms that have been suggested to explain the behavior of other pitch-control agents are very speculative. The anionic polymers that are sold as pitch-control agents presumably stabilize dispersed pitch particles. This hypothesis fits the established surface and colloidal properties of these materials.

Alum has long been used in the paper industry to solve problems associated with pitch deposition. Alum is also used in rosin sizing to form a cationic complex with rosin, which is then anchored onto fibers. It therefore seems reasonable to assume that alum reduces pitch deposit formation by transporting pitch out of the system.

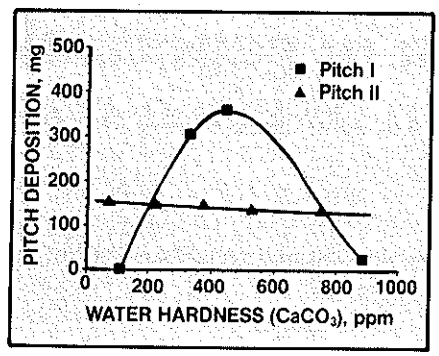
Talc has been found to have an effect by adsorbing pitch or by being adsorbed onto dispersed pitch.

There is a strong relationship between concentration of dispersed pitch and the extent of pitch problems occurring on the paper machine (*2*). This suggests that pitch deposition will decrease if the concentration of pitch particles is reduced by the use of alum (*16*) or a suitable polymer (*1*).

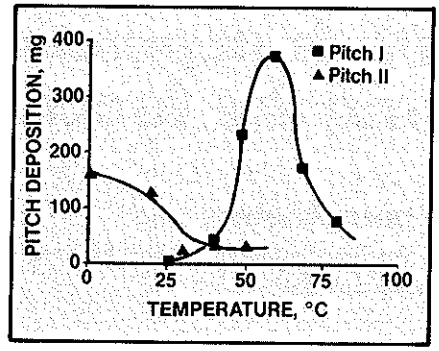
1. Particle size distribution of pitches I and II



2. Pitch deposition as a function of water hardness. Conditions: Pitch I = 50°C; pH 8.0; 2400 ppm pitch; 20-min duration. Pitch II = 20°C; pH 3.0; 800 ppm pitch; 3-min duration



3. Pitch deposition as a function of temperature. Conditions: Pitch I = pH 8.0; 540 ppm $CaCO_3$; 1200 ppm pitch; 20-min duration. Pitch II = pH 3.0; 225 ppm $CaCO_3$; 1000 ppm pitch; 3-min duration



It has been assumed that alum, as well as the synthetic cationic polymers used to reduce problems of this nature, obtain their effect solely by retaining colloidal pitch particles on the fibers. With the sophisticated retention systems available today, good first-pass retention can be achieved, with the result that the concentration of dispersed pitch is often quite low. However, our experience shows that a mill with an efficient retention-aid system and a low concentration of pitch particles can still have serious problems with pitch deposition.

Cationic polymers have been used to remedy pitch problems on machines with low concentrations of pitch particles. This suggests that the presumed mechanism of pitch control—the retention of dispersed pitch particles onto fibers—is not sufficient to explain the action of cationic polymers. This finding prompted us to conduct a series of experiments to study how these products affect the tendency toward pitch deposition.

Experimental approach

Pitch deposition is promoted by high shear forces (*3*). A Vibromixer can be used to induce shear forces for laboratory evaluation of a pulp's tendency to form pitch deposits (*20*). The Vibromixer is also useful for examining the process liquid (after fiber removal by filtration) or the white water (*2*), but then only the effect of the dispersed resin can be measured.

There is significant evidence (*2, 21*) that pitch in its dispersed form is the predominant cause of deposit formation. The suggested modes of deposition of dispersed resin (*1*), either by shear, flotation, or creaming, do not involve an interaction with fibers, but fibers may interact with dispersed pitch in several ways.

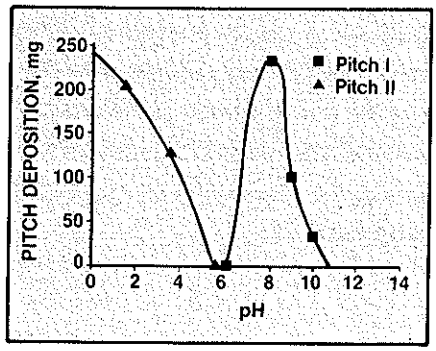
Pitch is adsorbed, to some extent, onto the fibers. It is likely that this adsorption depends on properties of the aqueous phase (pH and ionic strength). Pitch deposits can also be transferred to the fiber surface as the fibers brush past these deposits on the machine (*1*). Additives can also affect the extent of pitch adsorption onto fibers. Anionic low-molecular-weight polymers disperse resins and reduce the amount of pitch that is adsorbed onto the fiber surface. Cationic polymers, on the other hand, help retain pitch on the fiber surface. Thus, pitch deposition in a system containing fibers is a complex phenomenon influenced by multiple factors.

Pitch deposition cannot be effectively evaluated in a system containing fibers because the interaction of several effects makes it impossible to relate changes in the amount of deposited pitch with a single parameter.

The specific interaction between colloidal pitch and fibers can be studied by other methods. In an effort to study only the properties of dispersed resin, we used a system without fibers and added fibers only in certain cases.

The average particle size for both of the synthetic colloidal pitch dispersions used in these experiments (pitches I and II) was approximately 0.3μm. The particle size distributions for pitches I and II are depicted in **Fig. 1**. Allen (*2*) determined the particle size distribution of dispersed pitch for a number of pulps and found in all cases an average particle size of approximately 0.7μm, which is somewhat greater than that of the synthetic pitch dispersions used in these experiments but still of the same order of magnitude.

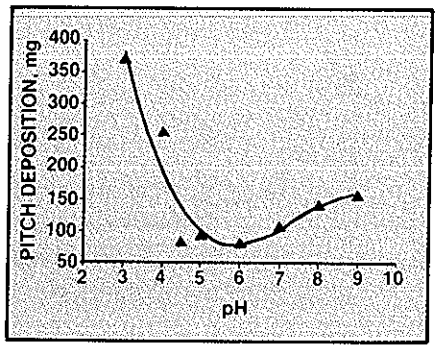
4. Pitch deposition as a function of pH. Conditions: Pitch I = 50°C; 543 ppm $CaCO_3$; 1200 ppm pitch; 20-min duration. Pitch II = 20°C; 0 ppm $CaCO_3$ (no hardness); 1000 ppm pitch 5-min duration



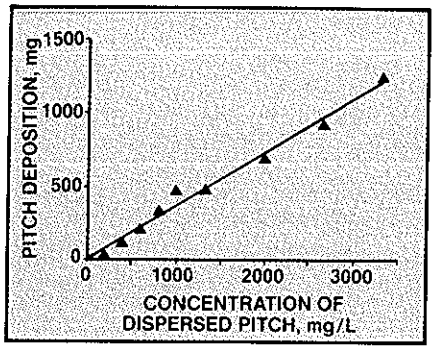
Deposits of pitch I were a mixture of free fatty acids and their calcium soaps. The 13.1% portion of the deposit that was extractable with neutral acetone corresponds to the content of fatty acid in acid form. X-ray fluorescence revealed 6.7% (weight-weight) of calcium, corresponding to 103% soap [$Ca(Soap)_2$].

The organic portion of deposits formed from kraft pulp is composed predominantly of free fatty acids and the calcium soaps of these fatty acids (*22*). Calcium carbonate is also usually found(*22*), at least in pulp mill screening rooms, as an inorganic moiety of a deposit. However, we believe that the deposits and the relationships found governing the extent of deposition of pitch I are of some relevance

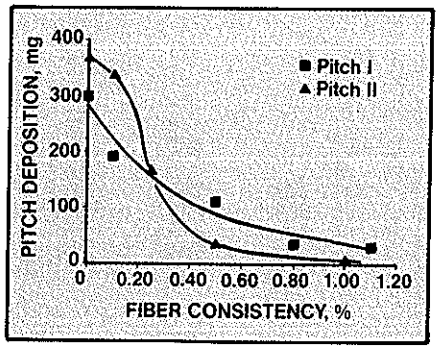
5. Pitch deposition (pitch II) as a function of pH. Conditions: 20°C; 225 ppm $CaCO_3$; 1000 ppm pitch



6. Pitch deposition (pitch II) as a function of the concentration of dispersed pitch. Conditions: 20°C; pH 3.0; 225 ppm $CaCO_3$



7. Pitch deposition as a function of fiber consistency. Conditions: Pitch I = 50°C; pH 8.0; 375 ppm $CaCO_3$; 1200 ppm pitch. Pitch II = 20°C; pH 3.0; 225 ppm $CaCO_3$; 1000 ppm pitch



I. Deposit formation of pitch II in water at various salt concentrations

Ionic strength, mole NaCl/L	*Deposit weight, mg*
0	215
0.01	308
0.1	394
1.0	436

in the manufacture and use of kraft pulp.

Deposits of pitch II were identical to the synthetic pitch that was prepared for dispersion, as determined by their identical infrared spectra. It is believed that pitch II is of relevance for systems using a pulp prepared by a neutral process, as it mainly constitutes an ester-type pitch. Esters are hydrolyzed in the kraft process and are not found in kraft pulp resins.

The main advantage in studying two different pitches, however, was the additional insight into the mechanism of deposit formation.

Effect of system parameters on deposit formation

Water hardness, temperature, pH

Pitch I. The effect of water hardness on formation of deposits of pitch I is depicted in **Fig. 2** for water at pH 8.0 and 50°C. Results of this investigation show that formation of the calcium soap of the fatty acid is necessary for pitch I to deposit. Formation of a fatty acid calcium soap requires an alkaline pH and, of course, presence of calcium. These laboratory experiments show that increased water hardness will increase deposit formation of pitch I. The results also show that there is an optimal ratio of calcium to pitch and that once this ratio is exceeded, pitch I becomes less prone to deposition. However, it has been found that increased water hardness in kraft pulp mills increases the deposition of pitch (*23*). Consequently, it is assumed that in practical applications, the ratio of calcium to fatty acid at which the level of deposit formation is most severe is not exceeded.

Figure 3 shows the strong effect of temperature on formation of pitch I deposits, with a maximum deposition at 60°C. At 40°C and 90°C, the level of deposition was only about 15% of that formed at 60°C.

Several authors (*3–6*) have suggested that resin deposition is dependent on the viscosity of the pitch and that little or no deposit is formed when the viscosity of the pitch is low. At increased viscosity, increased formation of pitch deposits is obtained. There is, therefore, an optimal resin viscosity for pitch deposition such that when this viscosity is exceeded, the pitch again becomes less prone to deposition. Although we have not made any attempts to characterize the pitch deposited with regard to its physical properties, we think that it is possible that our results generally comply with this theory. The deposit formed at the optimal ratio of calcium to fatty acid is tacky, while deposits formed at conditions deficient in calcium are comparatively less tacky and more fluid in nature. When calcium is added in excess of the optimal amount, the deposit becomes less tacky and more brittle, which correlates well with its decreased tendency to form deposits.

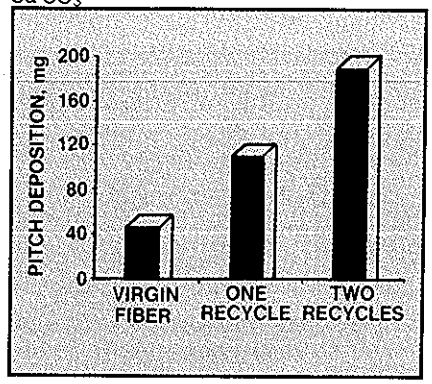
The variation in viscosity with changes in temperature can explain the pronounced temperature dependence with regard to resin deposition found in our experiments. At low temperatures, the viscosity is too high for deposit formation. However, when the pitch softens at increased temperature, deposits are formed. After the optimal viscosity for deposit formation has been attained, the pitch becomes more fluid on further increase of temperature and the extent of deposit formation decreases again.

Figure 4 depicts deposit formation of pitch I at varying pH. The pH of the system showed a profound influence on resin deposition, and no deposit was formed below pH 6.

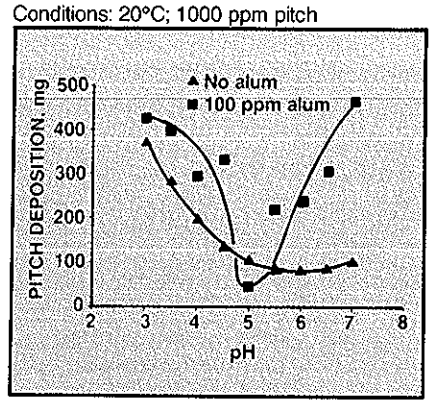
The pH exerts a great deal of influence on the state of fatty acids. It is assumed that, at a pH other than optimal, the ratio of free fatty acid to fatty acid calcium soap is altered, resulting in changed resin viscosity. It has been reported that low pH (below 6) at kraft pulp screening reduces deposit formation considerably (*24*). At pH lower than 6, the fatty acids are only marginally ionized and calcium soap is not formed. It has also been found that calcium soaps of fatty acids are not formed at pH above 10 (*22*), which explains the absence of pitch deposition at pH 10 and above.

Pitch II. Pitch II, which comprises an inherently tacky mixture of esters

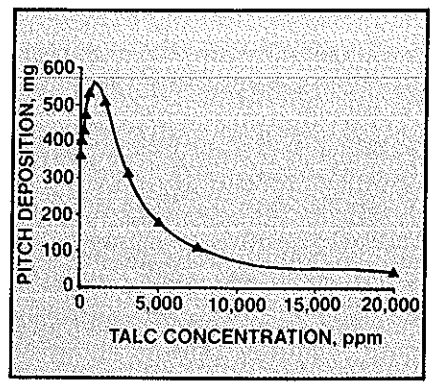
8. Pitch deposition as a function of fiber recycling. Conditions: fiber consistency, 0.8%; 50°C; pH 8.0; 1200 ppm pitch (type I); 225 ppm Ca CO_3



9. Pitch deposition (pitch II) over pH range 3 to 7 with 100-ppm concentration of alum in the furnish and with no alum in the furnish. Conditions: 20°C; 1000 ppm pitch



10. Pitch deposition (pitch II) as a function of talcum concentration. Conditions: 20°C; pH 3.0; 225 ppm $CaCO_3$; 1200 ppm pitch



of rosin, does not require any specific water hardness for deposition at acid pH. Figure 2 depicts the insensitivity of deposit formation of pitch II with regard to water hardness at pH 3.0. Pitch II is tacky at low temperatures but becomes more fluid at increased temperatures. This is also reflected in its reduced tendency for deposition at increased temperature, seen in Fig. 3.

The tendency for deposition of pitch II relative to pH is depicted in Fig. 4 and **Fig. 5**. Pitch II was found to be less prone to deposition at higher pH, a fact that we assume is related to the presence of fatty acid in pitch II. The fatty acid is added to form dispersed particles of the esters of rosin when added to water. It is assumed that the fatty acids of tall oil act as an emulsifier at higher pH, thereby preventing pitch deposition. However, deposits will form under alkaline pH conditions if there is sufficient water hardness in the system. The water hardness promotes formation of fatty acid calcium soap, thus presumably eliminating the emulsifying properties of the fatty acids, as seen in Fig. 5. Alternatively, the calcium fatty acid soaps may alter the tackiness of the resin, making it more prone to deposition. This illustrates the complexity of the parameters governing the deposition of pitch. Even in a simplified laboratory system, deposit formation is not governed solely by resin viscosity.

Salt concentration

The importance of the ionic strength of the aqueous phase on the extent of deposit formation was evaluated using pitch II. Sodium chloride was added to obtain the desired ionic strength. Results are presented in **Table I.** Increased ionic strength was found to aggravate deposit formation.

Pitch concentration

The concentration of dispersed pitch is an important parameter governing the extent of pitch formation. Allen (*2*) established a linear relationship between colloidal pitch concentration and lost machine time.

The importance of pitch concentration with regard to deposit formation was evaluated using pitch II. A linear relationship between concentration of dispersed pitch and deposit formation was found, as seen in **Fig. 6.** This finding supports Allen's assumption that lost time is not related to the concentration of dispersed pitch but, rather, to the rate of deposit formation.

Fiber concentration

Figure 7 depicts the relationship between deposit formation and fiber concentration. We found that deposition decreased as furnish consistency increased, which is contrary to findings by Farney (*25*). We assume that the virgin fibers used in our experiments adsorb pitch, thereby reducing the concentration of dispersed pitch. This assumption is supported by the results in **Fig. 8,** which show that the ability of fibers to reduce deposit formation is progressively reduced by recirculation of the fibers.

The use of recycled fibers in a papermaking process is often accompanied by the deposition of adhesives and other resinous materials in the fiber source. Deposition is usually drastically exacerbated when the proportion of secondary fiber to virgin fiber exceeds 2:1 or 3:1. This increased deposition is not necessarily caused by the increased concentration of depositable material. It could also be related to the low levels of virgin fiber in the stock. A low level of virgin fiber might be unable to adsorb a sufficient amount of the depositable material released from recycled fiber.

Alternatively, it may be that at high levels of consistency, the deposits that form are brushed off by fibers, as suggested by Allen (*1*).

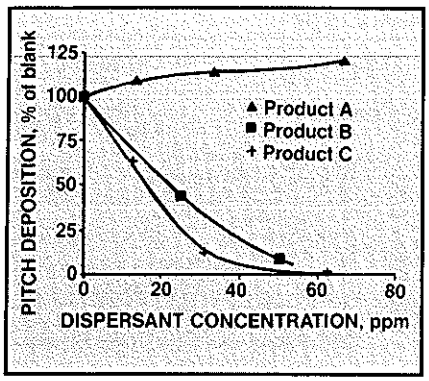
II. Performance of anionic polymers in controlling pitch formation

Additive	*Concentration, ppm on aqueous phase*	*Reduction in deposit formation, %*
Lignosulfonate	50	20
Polymerized naphthalene sulfonate	25	57
	100	75

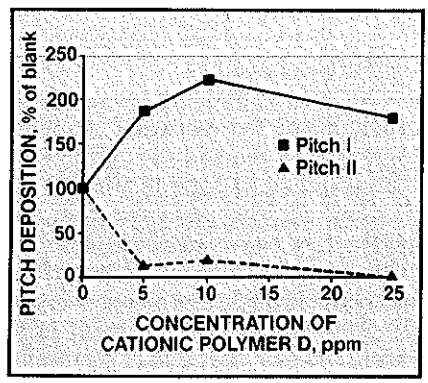
Effect of deposit-control agents

Chemical additives are often used successfully to prevent deposition of pitch in paper machine systems. Alum is a well-known remedy, used especially at acid pH. Talcum also is often successfully used to reduce pitch

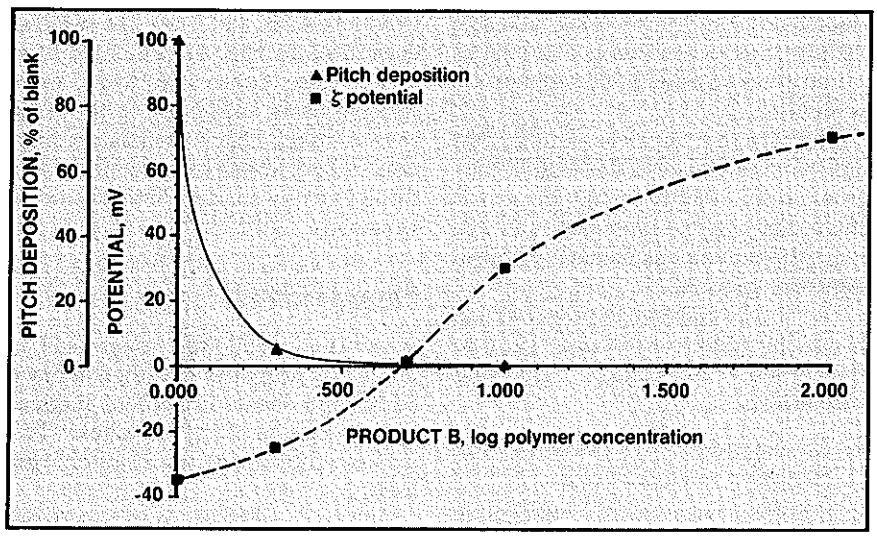
11. Efficiency of three dispersants in limiting pitch deposition (pitch I). Conditions: 50°C; pH 8.0; 455 ppm $CaCO_3$; 1200 ppm pitch



12. Efficiency of a single dispersant (product D) in limiting pitch deposition



13. Pitch deposition (pitch I) and ζ potential (electrophoretic mobility) as a function of product B concentration



deposition.

Anionic dispersants were widely used for awhile, but their use has declined considerably during the last ten years. There are several reasons for this decline. They sometimes impaired paper properties, such as opacity, and compromised the performance of certain additives, such as retention aids and sizing agents. The closure of mill water systems also raised concerns about the use of anionic polymers since, by their postulated mode of action, they would promote the accumulation of pitch in the mill water systems. But reductions in the use of anionic polymers is mostly the result of limited performance that did not justify the cost of treatment. However, the use of certain cationic polymers for deposit control is a developing trend.

Alum

Alum is sometimes used successfully, particularly in the acid range, to attenuate pitch problems. Alum retains dispersed pitch, and Allen (*16*) has investigated the parameters influencing its efficiency with regard to this effect. The aqueous equilibrium of alum is quite complex, and aluminium will be in different forms depending upon, for instance, the system pH. The efficiency of alum in reducing pitch deposition over the pH range at which paper is produced was investigated using pitch II. This pitch was chosen because it can be deposited throughout the whole pH range, provided some hardness is present (see Fig. 5), while pitch I only deposits in the pH range 6-10.

Figure 9 shows pitch deposition in a system with no alum and in a system with 100 ppm alum. Surprisingly, alum actually increased the deposition of pitch II throughout the pH range of investigation except at pH 5, where deposit formation was slightly reduced. Water hardness increased deposition of pitch II at alkaline pH, presumably by the formation of calcium fatty acids soap, which either increases the tackiness of the pitch or, alternatively, eliminates the emulsifying properties of the free fatty acids.

It is assumed that alum, in this system, performs a similar role, further aggravating deposition. However, it is possible that for a different type of pitch, alum might alter the physical properties of the pitch favorably, rendering it less prone to deposition.

Our work suggests that alum reduces deposition by removing dispersed pitch from the system. This is done by bonding the pitch to the fibers, as assumed by Allen (*16*).

Talcum

Talcum is the inorganic material most commonly used to reduce problems with pitch deposition. It presumably functions either by adsorbing pitch or by being adsorbed onto dispersed pitch. Specifically, the proposed mode of operation does not involve an interaction with fibers. The effect of the addition of micro talc is depicted in **Fig. 10**, again using pitch II. When added in small amounts, talcum increased the amount of deposition. The appearance of the deposit also changed and became grayer and less transparent, indicating incorporation of talcum in the deposit. The deposit formed at an addition of 1500 ppm talcum was analyzed with X-ray diffraction. We found 16% magnesium as MgO and 30.2% silica as SiO_2 (weight-weight), which corresponds to 50.6% incorporation of talc in the deposit. Further increase in addition of talc reduced the amount of deposition, but even at high levels of addition, i.e., 2% (seventeen times the concentration of pitch), there was still some deposition. However, this deposit was just a thin coverage of dust that would probably have been brushed off had fibers been present during the experiment.

It is apparently important to use a sufficient quantity of talc to reduce the formation of pitch deposits. If too little talcum is added it will not alter

the physical properties of the pitch to a sufficient extent. Instead, it will be incorporated in the deposit, causing a net increase in deposit formation.

Polymers

Anionic polymers. Anionic polymers used as pitch-control agents include lignosulfonates and the sodium salt of polymerized naphthalene sulfonate. These products had a limited effect at high concentrations, as seen in **Table II**, which is based on results of tests using pitch I.

Cationic polymers. A comprehensive range of cationic polymers of various type, molecular weight, and charge density were evaluated. Most of these products are experimental, but some are commercially available under the trademark Darasperse* and used as pitch-control agents in the paper industry. Quite remarkable effects were found with some of these polymers, as seen in **Fig. 11**. Products A, B, and C are all cationic polymers. Product A is an experimental polyquaternary polymer that increased pitch deposition. Products B and C both reduced deposition, with product C being the best of the two. These effects were obtained at addition levels comparable with those of other pitch-control agents used by the paper industry.

The cationic polymers' efficiency in preventing deposition varied considerably for the two different pitches used as model substances. **Figure 12** illustrates this. Product D efficiently reduced deposition of pitch II but significantly increased deposition of pitch I.

We did not expect to find that certain cationic polymers would be powerful aids in reducing pitch deposition. It was generally assumed that cationic polymers reduced pitch deposition simply by retaining dispersed pitch on the fibers, thus lowering pitch concentration in the system and reducing the tendency for deposit formation. While this is probably true, it is evident that these products perform yet another function, namely to stabilize dispersed pitch and prevent it from depositing. The concentration required for this stabilization is sometimes surprisingly low, and concentrations in the parts-per-million range are often sufficient to reduce deposition significantly. We cannot explain why one particular polymer reduces deposition of one type of pitch and yet aggravates the deposition of another.

The electrophoretic mobility (ζ potential) of the dispersed resin increases with the addition of the cationic polymer, as seen in **Fig. 13** for Product B. This indicates that the polymer is being adsorbed onto the pitch particles. The stabilizing effect of a cationic pitch-control agent on the dispersed pitch does not seem to be related to any particular electrophoretic mobility. Correlating the dispersed resin's ζ potential (relative to the deposited pitch) vs. the addition of a cationic pitch-control agent, as depicted in Fig. 13, reveals that a 98% reduction of deposition is obtained at a marginal change in electrophoretic mobility.

The fact that particle stabilization can be obtained at a decreased electrophoretic mobility of the dispersed pitch can only be interpreted in one way: the polymer is sterically stabilizing the particles.

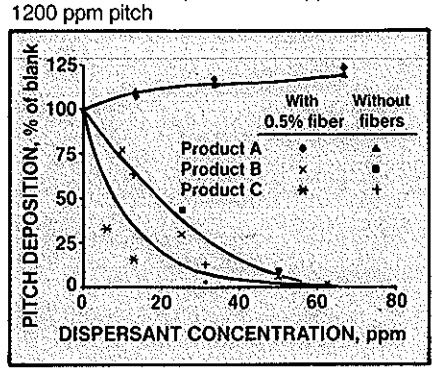
Our work suggests that the function of cationic pitch-control agents can be described by the following mechanism:

1. Adsorption of polymer on dispersed pitch particles
2. Stabilization of the dispersed pitch particles, thus preventing deposition
3. Fixation of the dispersed pitch particles onto fibers, thus reducing the concentration of pitch particles in the process water
4. Reduction in deposition proportional to the concentration of the remaining pitch particles.

Tests with fibers in the system

Figure 14 illustrates the relationship between cationic polymer concentration and pitch deposition, both with and without fibers present during the test. As depicted in Fig. 7, deposit formation is significantly reduced at the presence of fibers. This has to be considered in a comparison of the efficiency of polymers to reduce deposit formation with and without fibers present. Comparison has been made possible by normalizing both

14. Efficiency of three dispersants in limiting pitch deposition (pitch I) in a 0.5% consistency furnish and in a solution with no fibers. Conditions: 50°C; pH 8.0; 455 ppm $CaCO_3$; 1200 ppm pitch



sets of results to 100% for the two blank values (no polymer added). Products A, B, and C are the same as those used in Fig. 11. Their abilities to decrease deposition were, on a relative basis, unrelated to the presence of fibers. This is surprising, since some polymer loss by adsorption onto the negatively charged fiber would be expected.

Experimental

A synthetic colloidal dispersion of pitch was prepared and then subjected to high shear forces that induced the deposition of some pitch. Two different types of synthetic pitch were used.

One type, referred to in this paper as pitch I, was prepared using a method described by Farney (*25*). The potassium salt of distilled tall oil was dissolved in an isopropanol–water (1:0.05) solvent. This solution formed colloidal particles of tall oil when added to water.

The second type, referred to in this paper as pitch II, was chosen to be as different as possible from pitch I but still of relevance for the paper industry. Pitch II was prepared by dissolving a mixture of 90% glycerol ester of rosin and 10% potassium salt of tall oil in an isopropanol–acetone–water (1:0.6:0.05) solvent. The potassium salt of tall oil was included in the system as an emulsifier for the glycerol ester of rosin. This solution formed colloidal particles when added to water.

Deposition of pitch was induced by creating high shear forces using a Vibromixer, which consists of a stainless steel disc attached to a rapidly vibrating rod. The Vibromixer unit is

*Darasperse® is a registered trademark of W.R. Grace & Co.

used in TAPPI Routine Control Method RC 324 (*21*), which describes a method for determining depositable material in pulp and evaluating chemical deposit-control agents.

Experiments were typically performed as follows: Pitch solutions were added to a glass beaker containing 1 L of water at a known temperature and water hardness to obtain the desired concentration of pitch. Water hardness was adjusted by addition of calcium chloride. The pH was then adjusted with dilute hydrochloric acid or sodium hydroxide. Any additive under evaluation was always the last item to be mixed in. Some of the experiments were conducted on solutions containing unbeaten, bleached sulfate pulp fibers. The pulp fibers were always added before the pitch.

The glass beaker was placed in a water bath. Then a carefully cleaned, dried, and preweighed disc was attached to the Vibromixer and immersed into the aqueous colloidal pitch solution. The Vibromixer was switched on and run for the desired period of time (normally 5 min for pitch I and 3 min for pitch II). The disc was removed from the Vibromixer unit and dried in an oven to constant weight at 125°C. The amount of deposited pitch was calculated after weighing the disc on a high-accuracy balance.

Electrophoretic mobilities were determined with a REPAP Zeta-potential meter. Concentration of metals were determined by X-ray fluorescence. Particle size distributions were determined with a Coulter Model N4 instrument.

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