The importance of pH in controlling metal-soap deposition

L. H. Allen

The threshold pH value, below which metal soaps do not deposit, appears to be approximately 6.

In pulp and paper mills, metal-soap deposition is a topic that is often discussed, but little is known of the factors leading to it. Generally, these depositions consist of dissolved multivalent metal ions—usually Ca^{2+}, Mg^{2+}, Ba^{2+}, or Al^{3+} ions from the wood or from "hardness" in the water—reacting with the anion of the soap of a fatty or resin acid according to the equation:

$$\underset{\text{(Metal Ion)}}{M^{n+}} + \underset{\text{(Soap Anion)}}{n\text{Soap}^-} \rightarrow \underset{\text{(Metal Soap)}}{M\ \text{Soap}_n\downarrow} \quad (1)$$

The resulting metal soap, which is sticky and insoluble, is sometimes found in relatively large concentrations in pitch deposits. We have synthesized pure metal soaps (e.g., calcium oleate, aluminum oleate) and have found them to be exceedingly tacky, with a texture often resembling that of bubble gum. The metal-to-soap bond appears to be strong, so that the reaction depicted in Eq. 1 is effectively irreversible, even under moderately acidic conditions (e.g., pH 4).

Under what conditions does this happen? Traditionally, paper has been manufactured at acidic pH values, and the concentration of soap anions is low because they tie up with hydrogen ions to form insoluble fatty and resin acids:

$$\underset{\text{(Soap Anion)}}{\text{Soap}^- + H^+} \rightleftharpoons \underset{\text{(Fatty or Resin Acid)}}{H\ \text{Soap}\downarrow} \quad (2)$$

Consequently, chemical analyses of paper mill pitch deposits usually show little metal-soap content. Nevertheless, if the pH rises at some point in the process stream, appreciable concentrations of metal soaps are often found in the deposits.

Since concentrations of metal ions and of fatty and resin acids in mill white waters are usually appreciable, it is hypothesized that the extent of the reaction described in Eq. 1 is controlled by the presence or absence of soap anions in the white water and that this, in turn, is controlled by pH according to Eq. 2.

The objectives of the work described in this report were to:

- Determine the pH conditions under which a measurable concentration of soap anions can exist in mill pulps
- Assemble mill evidence to test the previously stated hypothesis.

Although the literature on pitch problems does not address the first objective directly, there is some evidence that increased deposition occurs at higher pH values, presumably because of metal-soap deposition. For example, Gustafsson *et al.* (*1*, *2*) found that, above pH 6, increased amounts of deposits were obtained from unbleached sulfite pulp on copper and stainless steel surfaces in a laboratory deposition apparatus. In addition, Swanson and Cordingley (*3*) observed that, in the presence of calcium ion, pitch films did not build up in multiple layers below pH 6. Finally, Affleck and Ryan's account (*4*) of pitch problems in the unbleached screen room of a kraft pulp mill shows that deposition increases substantially at pH values above approximately 6.

Nyren and Back (*5*) have calculated, from solubility products, the solubilities of several pure, saturated, carboxylic acid anions in water as functions of pH. The pH values at which lauric and myristic acids begin to dissociate appreciably are approximately 5 and 6, respectively. Unfortunately, these particular acids are present in wood resin only to a minor or almost negligible extent.

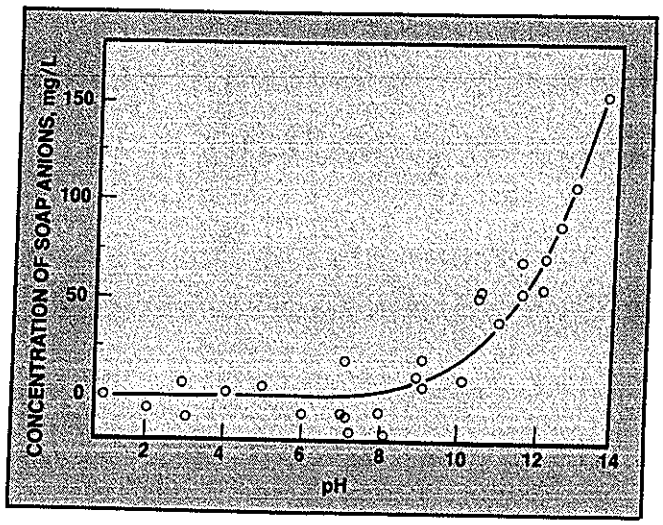
In 1970, Cratin and Murray (*6*) hypothesized, on the basis of surface tension measurements of "pitch solutions," that there is a dissociation of hydrogen ion from one of the components of the resin as the pH is increased from 5 to 10. This corresponds to the reaction in Eq. 2, going to the left. More recently, the precipitation of soap from brown white water, visible in an optical microscope as the pH was lowered below 8, was documented (*7*). The precipitated soap was observed to be a colloidal suspension of particles with dimensions approaching the limits of resolution of the microscope (approx. 0.5 μm). Moreover, evidence suggests that in a kraft mill bleachery, this finely dispersed suspension of fatty and resin acids heterocoagulates with fibers at low pH values (*8*).

Results and discussion

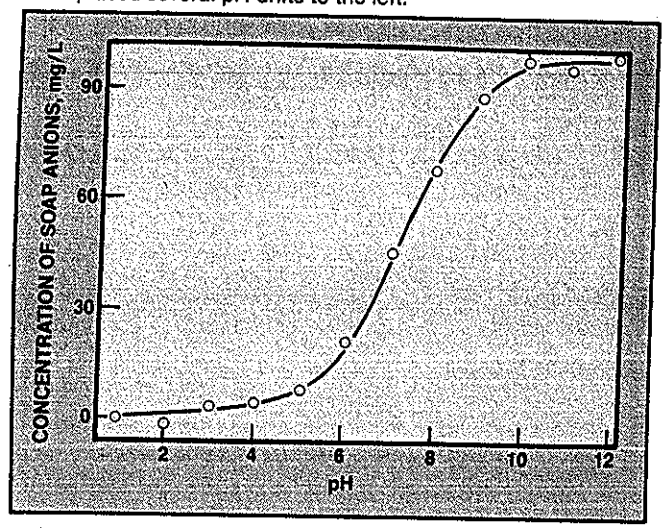
Figure 1 shows the concentration of soap anions in the white water of a newsprint paper machine as a function of pH over the range 1 to 14. Although there is considerable

Allen is the director of the Process Chemistry Division at the Pulp and Paper Research Institute of Canada, 570 St. John's Boulevard, Pointe Claire, Quebec, Canada H9R 3J9.

1. Concentration of dissolved soaps as a function of pH in white water from a newsprint paper machine. With increasing pH above 7, the soap anion concentration increased slowly at first and then more rapidly.



2. Concentration of dissolved soaps as a function of pH in unbleached-kraft screen-room white water. A rise in soluble soap concentration, similar to that in Fig. 1, was observed, but the curve is displaced several pH units to the left.



scatter in the results (obtained with a solvent-extraction technique), it is evident that the concentration of dissolved soap is low or negligible up to a pH of about 7. Above this, the soap anion concentration increases with increasing pH, slowly at first and then more rapidly.

A curve with a similar shape was obtained for screen-room white water from an unbleached kraft pulp mill, as seen in Fig. 2. In this case, however, the concentration of soap anions begins to increase at a lower pH and continues until, at a pH value slightly above 10, all the soap has dissolved. The pulp that provided the results in Fig. 2 was initially at pH 10.8. Thus we have a curve for the precipitation of fatty- and resin-acid from solution (Eq. 2, going to the right) as the pH is lowered from this value. Conversely, the data in Figure 1 document the formation of soap anions as they dissolve with increasing pH (Eq. 2, going to the left). Because Eq. 2 is a heterogeneous reaction, it is not surprising that the pH values at which the curves in Figs. 1 and 2 begin to rise are different for the two different directions of reaction, nor is it particularly surprising that the curve in Fig. 1 does not attain a maximum, even at pH values over 13. There are other factors possibly contributing to the differences between the curves in Figs. 1 and 2:

- Different pulps: the two types of pulp contain different amounts and kinds of dissolved and colloidal substances, such as lignin and hemicellulose
- Kinetic effects: some time may be required for the reaction to occur in either direction.

Clearly, there is a need for more research to sort out these factors.

In both Figs. 1 and 2, the dissolution/precipitation curves rise over a pH interval of 5 or more units. This is in contrast to most homogeneous acid/base reactions (Ref. 6, for example), where a species dissociates from approximately 0% to approximately 100% over 2 pH units. The reason, of course, for the wider pH range for the dissolution/precipitation reaction (Eq. 2) is that the reaction is heterogeneous in nature.

That the dissolution of fatty- and resin-acid soaps occurs during neutral and alkaline sulfite pulping is demonstrated by the data of Wearing *et al.* (*9*). In their work, a series of high-yield sulfite cooks was carried out on black spruce wood with liquors adjusted to a number of different initial pH values. The data in Table I, interpolated from graphs of their results, give the concentrations of dissolved fatty-and resin-acid soaps measured in the various spent cooking liquors at 80% and 90% yields. Clearly, at low pH, there is a negligible formation of soap anions and, at pH 5.5 and higher, there is considerably greater dissolution of resin — and fatty-acid soaps and, consequently, a higher concentration of soap anions. In all likelihood, the high temperature in the sulfite digester is responsible for the somewhat lower pH at which dissolution begins, relative to that in Fig. 1; it may also be responsible for the apparent maximum in soap concentration reached at pH 7.5.

Evidence from mills and applications of the concept

Case 1

A low-yield, sulfite/stone groundwood, integrated newsprint mill in eastern Canada encountered a pitch problem consisting of large amounts of sticky black deposits in the sulfite stock line after washing. Detachment and carry-over of the deposited material to the newsprint machine led to frequent sheet breaks and dirt specks in the product.

Measurement of pH around the mill showed the groundwood mill to be operating without deposits at pH approx. 4.5. However, because of rather alkaline mill water (pH 7.3–8.0) containing considerable concentrations of barium and calcium ions, the sulfite system was operating at a pH value above 6 and occasionally exceeding 7. Chemical analysis of the deposits showed relatively large amounts (17%) of barium and calcium soaps.

Successful solution of the problem consisted of using some paper machine white water, which was rich in alum and consequently at pH approx. 4.5, in the sulfite washers to bring the pH down to 4.5–5.0. It was reasoned that this suppressed the dissolution of fatty- and resin-acid soaps (Eq. 2, to the left) and eliminated metal-soap formation.

I. Concentration of dissolved soaps of resin and fatty acids, mg/L

pH*	80% Yield	90% Yield
1.9	3.0	2.5
3.2	3.0	2.5
4.5	3.0	2.5
5.5	19	15
7.5	85	45
12.5	85	45

*Initial pH of cooking liquor.

Case 2

A softwood bleached kraft pulp mill in western Canada was experiencing heavy deposition in the brownstock screen room. Subsequent detachment of deposits led to pitch-dirt in the final pulp and to plugging of screens and cleaners. The pH of the stock in this part of the kraft mill was over 10, and metal soaps constituted 30% of the deposited material. Clearly, from Fig. 2, conditions were ideal for metal-soap formation. Indeed, it has been shown that high concentrations of soap anions in this part of the mill generally lead to high rates of deposition (*10*), and a mechanism for the formation of metal soaps has recently been advanced (*11*). This mechanism proposes that soap anions are adsorbed onto calcium carbonate, which is also present in unbleached kraft pulps, and are then converted into calcium soaps. This mechanism is felt to be more feasible because the small amounts of dissolved calcium ion in unbleached kraft pulp appear to be unavailable for reaction because they are tied up with lignin.

The mill's problem was solved by acidifying the screen-room water with sulfuric acid to pH 6.0-6.5 in a manner similar to that described in another study (*4*). The unbleached part of this mill is now exceptionally free of deposits. The success may not be entirely attributable to the suppression of metal-soap formation because calcium carbonate, which was also a major component of the deposits, dissolves slowly at pH 6.

It is worth noting that acidification of screen-room water has been successful in many kraft mills. However, sometimes it is not possible to use this technique because excessive foaming of the stock is encountered or because the grouting of the tiles in the chests, etc., may not be designed for the lower pH.

Case 3

In recent research (*8*), concentrations of dissolved soaps were measured at each stage of manufacture in six fully bleached kraft pulp mills. In all cases, the concentrations of dissolved soaps were negligible in bleaching stages at low pH values and appreciable at higher ones. Although no attempt was made to establish the lowest pH at which dissolved soaps occur, the data indicated that it was between 4.6 and 6.3.

Concluding remarks

Considerable evidence has been presented suggesting that the formation of metal soaps, which contribute to pitch deposits, is controlled by the availability of dissolved soap anions which, in turn, is controlled by pH. Concentrations of dissolved soap anions measured in newsprint stocks at various pH values (Fig. 1) suggest that pH values above 7 will be especially detrimental. However, it is quite possible that metal-soap formation occurs in the presence of dissolved-soap concentrations too small to be measured by our technique. Therefore, a more conservative threshold, such as pH 6, probably constitutes a better guideline for pitch control. Certainly, the film-deposition (*3*) and surface-tension (*6*) evidence in the literature suggests that pH 6 might be a better threshold.

In unbleached kraft pulp mills, there is ample evidence that pH less than 6.5 appears to be adequate to suppress metal-soap deposition in the brownstock screen rooms.

A discussion of the effect of pH on pitch deposition would not be complete without mentioning that pH often affects the colloidal stability of the dispersed resin (*7, 12*). In addition, the stabilities of other forms of depositable material, such as defoamer residues and "stickies" from recycled paper, are influenced by pH. In the case of dispersed material, pH almost always affects the charge on the dispersed particles (*7,13*). For example, we know that in kraft pulp mills, the colloidally dispersed resin heterocoagulates onto the fibers at pH less than 3 (*8*). Moreover, if alum is used in papermaking, pH strongly affects the hydrolysis and formation of polymeric aluminum hydroxy sulfates, which cause the colloidal flocculation. This has been investigated at length for newsprint (*14-16*), and optimum pH values and alum concentrations have been established. Finally, in fine-paper mills, the presence of large amounts of clay and/or calcium carbonate can affect deposition, because it is known that soaps adsorb on calcium carbonate (*11*). In addition, preliminary work in our laboratory has shown that dispersed resin particles adsorb on clay particles. Both of these phenomena may be pH-dependent.

Experimental

Materials

Paper machine white water from an eastern Canadian newsprint mill making letterpress-grade paper from a spruce/balsam fir wood species mixture (25% sulfite; 75% stone groundwood) was used in obtaining the results depicted in Fig. 1. The results in Fig. 2 were based on a sample of unbleached screen-room white water from an eastern Canadian, fully bleached hardwood, kraft pulp mill. A similar curve was obtained with a sample from a softwood mill (*10*). The pH was adjusted by dropwise addition of concentrated HCl or NaOH, as necessary.

Procedures

Concentrations of dissolved soap anions in mill white waters were determined by performing two extractions. For Fig. 2, these were done using a modification [described in (*10*)] of the procedure developed by Saltsman and Kuiken (*17*) for estimating the amount of tall oil in sulfate

black liquor. In recent years, we have established that the additions of hydrogen peroxide and sodium sulfite, part of the original procedure (*17*), are not necessary for white waters. The results in Fig. 1 were obtained using further modifications, described as follows.

In the first extraction, the sample was acidified to pH 1 to precipitate all the soaps as acids, in which form they can be extracted with petroleum ether. A second extraction was then performed at the pH of the experiment, to provide a measure of the amount of water-insoluble colloidal resin. (In all cases the extraction was done within 30 min of the pH adjustment.) The difference between the two extractions gives the amount of soluble soaps at the pH of the experiment.

For each extraction, the procedure was as follows:

- Measure 250 mL of the white water sample into a 400-mL beaker.
- First extraction only: acidify with hydrochloric acid to a pH of 1 (equal parts of concentrated hydrochloric acid and water).
- Second extraction only: adjust pH to desired value.
- Transfer the mixture to a 1-L separatory funnel.
- Add 250 mL acetone and 60 mL methanol and shake well.
- Add 200 mL petroleum ether and shake for 10 min.
- Allow phases to separate.
- Drain aqueous layer.
- Wash ether layer twice with 50-mL portions of a 1:2:1 water:acetone:methanol mixture, and add the washings to the aqueous phase.
- Drain ether layer.
- Extract aqueous layer a second time with 200 mL petroleum ether, as described previously.
- Combine ether layers from both extractions.
- Evaporate ether on a rotary evaporator.
- Freeze-dry the sample overnight and weigh the residue.

Literature cited

1. Gustafsson, C., Norsk Skogind. 8(2): 54(1954).
2. Gustafsson, C., Tamella, V., and Lindh, T., Paper and Timber (Finland) 36(6): 269(1954).
3. Swanson, J. W. and Cordingley, R. H., Tappi 31(10): 684(1956).
4. Affleck, R. R. and Ryan, R. G., Pulp Paper Mag. Can. 70(24): 107(1969).
5. Nyren, V. and Back, E., Acta Chem. Scand. 12(6): 1305(1958).
6. Cratin, P. D. and Murray, J. M., Tappi 53(10): 1960(1970).
7. Allen, L. H., Pulp Paper Can. 76(5): T139(1975).
8. Allen, L. H. and Lapointe, C. L., "Physical Distribution of Resin in Bleached Kraft Pulp Mills," in press Pulp Paper Can.
9. Wearing, J. T., Ouchi, M. D., Mortimer, R. D., Kovacs, T. G., and Wong, A., J. Pulp Paper Sci. 10(6): J178(1984).
10. Douek, M. and Allen, L. H., Pulp Paper Can. 81(11): T317 (1980).
11. Douek, M. and Allen, L. H., J. Pulp Paper Sci. 9(2): TR48 (1983).
12. Allen, L. H., Trans. Tech. Sect. CPPA 3(2): 32(1977).
13. Strazdins, E., Tappi 55(12): 1691(1972).
14. Allen, L. H., Trans. Tech. Sect. CPPA 6(1): TR8(1980).
15. Allen, L. H., Pulp Paper Can. 82(11): T397(1981).
16. Allen, L. H., Trans. Tech. Sect. CPPA 8(4): TR85(1982).
17. Saltsman, W. and Kuiken, K. A., Tappi 42(11): 873(1959).

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