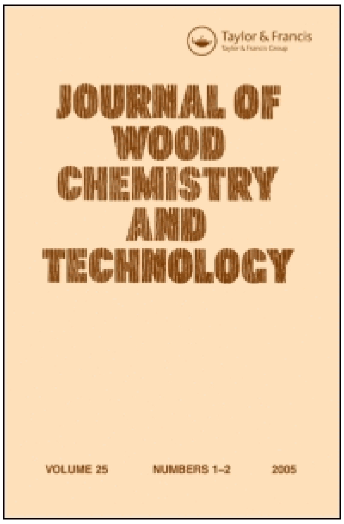

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DISPERSED RESIN IN BLEACHED KRAFT PULP MILLS

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ABSTRACT

Several properties of the dispersed resin in bleached kraft pulp mills have been investigated. Average concentrations of resin particles in filtrates of pulps from various points along the process stream are reported. For each sampling location, the change in particle concentration with time of pulp sample storage at 5°C has been determined. In the future, this will enable rough estimation of original concentrations when samples must be measured a few days after collection. Size distributions of resin particles were the same at all sampling points, from which it follows that, in practice, the relationship between concentration and deposition rate is relatively unaffected by size distribution. Dispersed resin particles were negatively charged throughout the mills. The low charge observed in C-stage pulps was insufficient to confer stability, which further supports the hypothesis that the dispersed resin is heterocoagulated with the fibers in this acidic stage.

INTRODUCTION

A decade has now passed since the "pitch count" procedure, for measuring dispersed resin concentrations in pulps and white waters, was first introduced to the pulp and paper industry[1]. During this time its satisfactory performance has led to its adoption as a CPPA Useful Method[2].

The technique provides a rapid way (<0.5 h per measurement) to measure particle concentrations of dispersed resin in process liquids. Generally, if dispersed resin is causing the problem, the rate of deposition or degree of difficulty is proportional to the particle concentration[1]. Ranges of particle concentrations in various kinds of mill have now been established[3] and a survey of concentrations in the bleacheries of six fully bleached kraft pulp mills has recently been completed[4].

The pitch count procedure has proven useful: as a diagnostic tool for mills when they encounter pitch problems; as a method of monitoring dispersed resin concentrations during periods when especially resinous wood is used, white water recirculation is increased, or mill trials with additives are conducted; and as a means for determining optimum concentrations of certain pitch-control additives.

In the unbleached screenrooms of kraft mills, where serious deposition can occur and lead to dirt problems, the resin particle concentration is but one of five factors which can influence the rate of pitch deposition. The others include concentrations of dissolved soaps, suspended $CaCO_3$, dissolved Na_2CO_3 and brown-stock defoamer. Laboratory procedures have been developed for measuring concentrations of these other materials (screenroom soaps[5], $CaCO_3$ in white liquor[6], Na_2CO_3 in white liquor[7] and defoamer[8]). Our experience suggests that the rate of deposition is proportional to any one of these concentrations if the others are held constant.

Deposition problems can also occur in the bleachery and pulp machine areas of kraft mills. Over the years the pitch-count procedure has proven useful for monitoring dispersed resin particle concentrations in these locations.

With time, a number of questions have arisen:

1. How does resin particle concentration vary from one sampling point to another in a kraft mill bleachery?
2. If a pitch count cannot be done right away, can the samples be stored under refrigeration and counted later? If so, is there a drop in concentration with time?
3. Does the size distribution of the resin particles affect the relationship between pitch count and deposition rate?
4. Does the charge on the resin particles affect the pitch count?

The objectives of the work described in this paper and a previous one[4] were to determine answers to these. In Reference 4 measurements relating to the first question were reported.

RESULTS AND DISCUSSION

How the dispersed resin particle concentration changes as the pulp proceeds through the various stages of processing in a fully bleached kraft pulp mill is shown in Figure 1. The bars denote average concentrations calculated from the results in Reference 4 of the four mills (2 softwood and 2 hardwood) with a CEDED bleach sequence. In the kraft digester, over half of the resin is saponified; of the remainder, much is attached to fibers and fines, but some is emulsified. In the unbleached part of a mill, resin is dispersed by: the mechanical action of the liquor circulation pumps, agitation in the lower cooking zone, hydrodynamic shear at the blow valve and agitation at the knotters, screens, cleaners and stock pumps. By the time the pulp reaches the brownstock decker, washing has already greatly decreased the concentration of dispersed resin in the process liquid around the fibers.

There is a large decrease in the resin particle concentration when the pulp goes from the brownstock decker vat to the C stage.

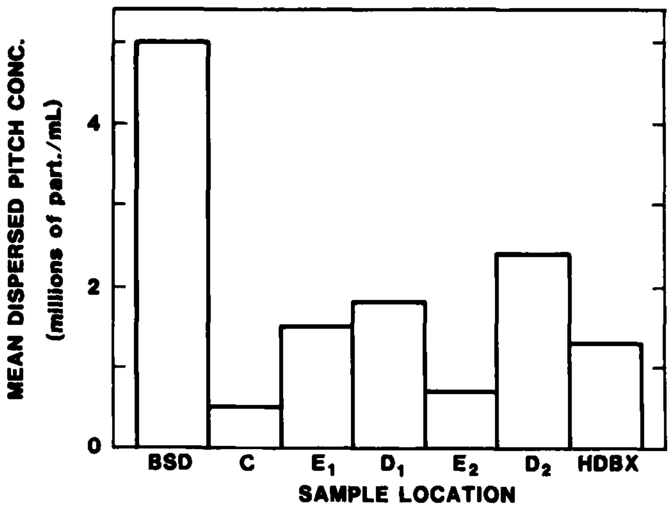

FIGURE 1: Average dispersed pitch particle concentrations at various points in the process streams of 4 fully bleached kraft pulp mills. Samples were taken from the vats of the various washers and decker. Concentrations were highest in the unbleached pulp and lowest in the C stage. (BSD = brownstock decker; HBX = pulp machine headbox)

Although some of this is attributable to dilution of the dispersed resin, most of the decrease is because the dispersed resin is coagulated by hydrogen ions present in large concentrations at the low pH values of the C stage. (pH values are given in Figure 4.) The coagulated resin which is not washed out at the C-stage washer is redispersed in the E_1-stage pulp[4]. Changes in resin particle concentrations in subsequent stages of bleaching have been discussed in Reference 4.

The decrease in resin particle concentration as a function of storage time in a refrigerator is given in Figure 2. As was observed for newsprint pulps[9], there was a relatively rapid initial decrease in concentration which slowed considerably after a

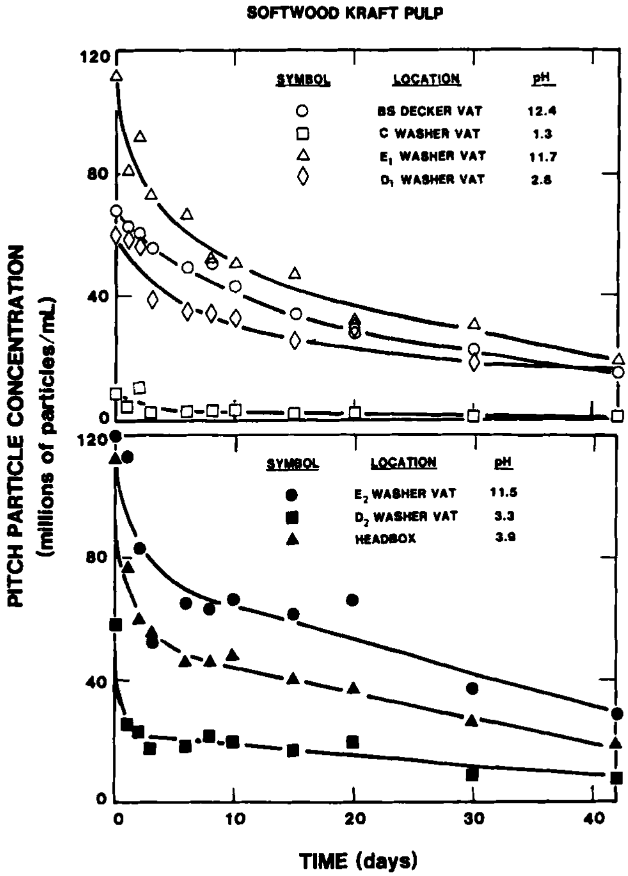

FIGURE 2: Pitch particle concentrations as a function of pulp storage time at 5°C for samples taken from various points in a softwood, fully bleached kraft pulp mill.

few days. Half-lives (time required for a particle concentration to fall to half of its original value) interpolated from Figure 2 are shown in Table 1; they range from 1.5 to 15 days. The half-life for resin particles in newsprint pulps is approximately 5 months[9]. Thus, the particle concentration drops considerably faster in kraft pulps than newsprint ones. The difference is probably attributable to the modes of stabilization of the dispersed

TABLE 1

SAMPLE	HALF-LIFE (days)
Brownstock Decker	15
C	11*
E_1	8.0
D_1	11
E_2	14
D_2	1.5
Pulp Machine Headbox	3.0

* Estimate for the few resin particles which did not coagulate.

material in these two kinds of pulp. Newsprint dispersed resin has been shown to be stabilized sterically[9], whereas kraft dispersed resin is stabilized by the charge on the particles[10].

The results in Figure 2 suggest that it is best to measure resin particle concentrations in kraft pulps immediately after sampling. If a pulp sample must be stored in a refrigerator prior to a pitch count, an estimate of the original concentration can be made from the appropriate curve in Figure 2, assuming that there is no mill-to-mill variation for the curves in this figure.

Resin particle size distributions measured at various locations in two mills, one using softwoods and the other hardwoods, are given in Figure 3. The distributions in the two mills were similar, although in the hardwood mill there appeared to be slightly larger amounts of particles with larger diameters. Within either mill the particle size distributions remained the same for all of the various stages of processing. It is interesting that the resin particle size distributions are very similar to those reported previously for stone groundwood and sulfite pulps[1].

Because the size distribution measurements were done upon return of the samples to our Pointe Claire laboratory and the

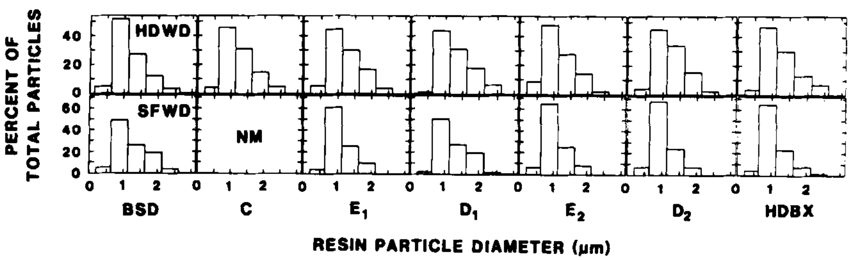

FIGURE 3: Size distributions of resin particles in samples taken from various points in a hardwood (top) and a softwood (bottom) fully bleached kraft pulp mill. Within experimental error, the size distributions were identical at all stages of processing, both in the softwood and hardwood mills. (NM = not measured)

measurements required considerable time, the results in Figure 3 were obtained from 2 to 18 days after sample collection. We were able to confirm by separate measurements that there was no difference between size distributions measured 2 and 18 days after collection. It is, however, probable that some of the larger particles are lost during the first two days, as this is usually the case for dilute oil-in-water emulsions.

Over the years we have occasionally received comments from people making pitch count measurements in mills that the particle size distribution can vary considerably. The results in Figure 3 tend to confirm our earlier assertion[1] that the size distribution does not vary very much. It would follow that, in practice, the relationship between pitch count and deposition rate remains relatively unaffected by size distribution.

Shown in Figure 4 are the electrophoretic mobilities of resin particles in samples from various locations in six fully bleached kraft pulp mills. (Electrophoretic mobilities are roughly proportional to the charge on the dispersed particles.) It is evident

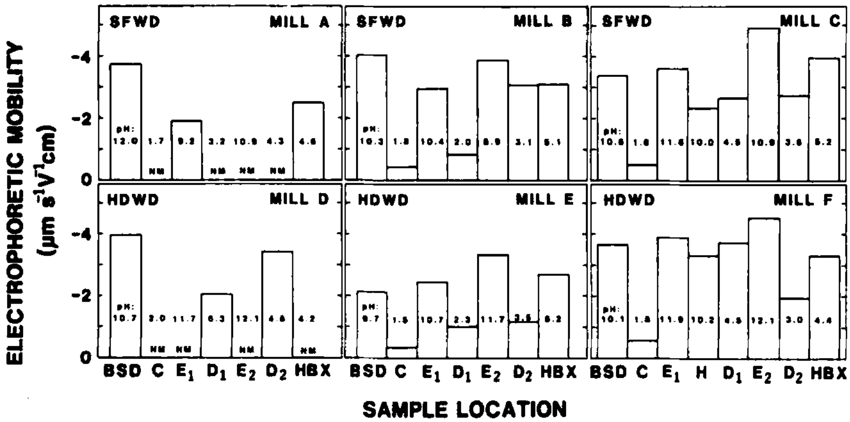

FIGURE 4: Electrophoretic mobilities of dispersed resin in samples taken from various points in 6 fully bleached kraft pulp mills. Mobilities, and hence the charge on the resin particles, were consistently negative. The mobilities of the C-stage pulps were probably insufficient to confer stability on the resin particles, as is also evident in Figures 1 and 2. (NM = not measured; figures inside bars indicate pH)

from Figure 4 that the resin particles were consistently negatively charged. Moreover, the charge is considerably higher than normally found in newsprint pulps[9], which is in keeping with the concept that the resin particles in kraft pulps are charge stabilized[10]. In addition, the charge on kraft mill resin particles appears to be primarily dependent on pH, at low values, and varies with pH in a way similar to that of kraft fines, as reported by Strazdins[11]. At pH values over 3, other factors appear to play a role in determining particle charge.

The mobilities of the resin particles in the C-stage pulps were probably insufficient for them to be stabilized by charge; this is further substantiated by the conclusion reached in an earlier publication[4] that when the pulp is acidified for the C stage, the dispersed resin loses its stability when the carboxylic acid groups, which confer charge, protonate.

There appears to be no correlation between particle charge and the half lives of the dispersed resin particles at the various points of sampling.

EXPERIMENTAL

MATERIALS

Pulp Samples:

Pulp samples were obtained from eastern Canadian mills which were not having pitch problems at the time of sampling. They were taken from the vats of the brownstock decker and washers, all within a period of approximately an hour, in each mill. Pulp consistencies were in the range from 1 to 2%. Further details about the samples are available in Tables I to III of Reference 4.

The pulp samples for the work in Figure 2 were taken from a mill that was recirculating bleachery white waters to a greater than average extent; this was necessary to obtain sufficiently high resin particle concentrations for good accuracy in their measurement. The samples for Figure 3 were obtained from Mills A and D[4].

PROCEDURES

The full procedure for determining pitch particle concentrations has been published previously[1,2]. Prior to each pitch count the sample was filtered through a papermachine wire to remove most of the pulp fibers. Estimates of the accuracy of this kind of measurement are given in Reference 1. Average pitch particle concentrations (Figure 1) were calculated from measurements made at 4 mills and reported previously[4].

In the experiments where particle concentration was measured as a function of time, the pulps were stored in 4.5 L Nalgene bottles at 5°C. Before each measurement the pulp samples were gently agitated, to redisperse the resin evenly, by inverting the containers 10 times.

Electrophoretic mobilities were measured with a Rank Mark II electrophoresis apparatus as described previously[10].

Particle size distributions were determined with a Vickers projection microscope as described earlier[10].

ACKNOWLEDGEMENTS

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