Evaluation of a laser-optical resin particle counter

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ABSTRACT: A laser-optical particle counter for dispersed extractives (wood resin) was evaluated. The fluorescent intensities of dyed resin particles were measured as they passed through a laser beam in a hydrodynamically focused stream. The results were compared with those from a hemacytometer. The new instrument gave reproducible results for pulp filtrates after the procedure for dyeing resin particles was modified. The laser-optical counter usually gave a higher particle concentration than given by the hemacytometer because fines are often coated with wood extractives and the staining is not entirely selective. Some stained fines were indistinguishable from resin particles, but in pulp and paper mills, it is probably appropriate to count resinous fines as well, because these are found in pitch deposits.

Application: A new instrument should soon be able to measure on-line the concentrations of resin particles in white water and help mill personnel assess the impact of process changes on pitch control.

The particle concentration of dispersed pitch, or suspended wood resin, is an important factor for pitch control in pulp and paper manufacture. Although many factors can influence the rate of pitch deposition in a mill, the potential for the pitch in pulp to be troublesome is often proportional to the concentration of colloidal pitch droplets suspended among the fibers in the white water [1].

A reliable on-line method to determine the concentration of colloidal resin particles in white water would be an asset for dealing with pitch deposition problems. Conventional methods of determining the concentration of dispersed wood resin include solvent extraction [2] and direct microscopic particle counting with a hemacytometer [1, 3, 4]. Although both techniques are widely used in research labs and pulp and paper mills, they suffer from the drawbacks of being off-line and time consuming.

BASF recently developed a laser-optical method for counting dispersed resin particles [5–8]. The method involves staining the resin particles selectively with a fluorescent dye and measuring the fluorescent intensity from the dyed particles. The instrument is still under development but is claimed to be a tool for evaluating the efficiency of aids for controlling pitch.

Paprican conducted an independent evaluation of the instrument with support from BASF personnel. Here, we will describe the use of this benchtop instrument and our assessment of its strengths and weaknesses. Our primary objective was to determine if the instrument can be used as a reliable and convenient tool for determining the concentrations of resin particles in pulp filtrates.

EXPERIMENTAL

Experiments designed to evaluate the instrument included:

- Making direct observations of dyed samples with a fluorescence microscope
- Counting the resin particles of some model systems with both the laser-optical particle counter and a hemacytometer
- Separating the pulp filtrate by centrifugation and analyzing the supernatant and the sediment with both the hemacytometer and the resin particle counter.

The laser-optical particle counter

Details of the operating principle of this instrument have been published elsewhere [5–8], and only a brief description will be given here.

Figure 1 is a diagram of the instrument. Suspended colloidal resin particles are stained with a fluorescent dye and separated and focused into a fine water jet, as shown in **Fig. 2** [9]. A focused laser beam with a wavelength that coincides with the excitation wavelength of the dye (442 nm) excites the stream of individual particles. The fluorescent signal of each particle is detected by a photomultiplier, amplified by a logarithmic amplifier, and counted and sorted according to the fluorescent intensity by a multichannel analyzer.

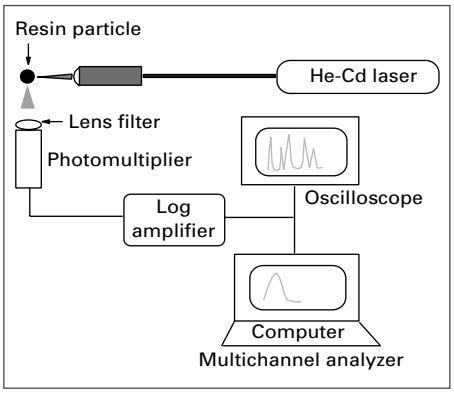
The higher channel numbers in the multichannel analyzer correspond to larger particle sizes. The channel numbers can be calibrated with a series of fluorescent latex particles of known size in the range of 0.5–5 μm. If only the relative changes of particle numbers and size distributions are of interest, it is sufficient to display data in channel numbers rather than in absolute particle sizes. In this report, both channel numbers and the estimated particle sizes are shown.

The instrument's speed and its potential for on-line analysis are expected to be its primary advantages. Depending on the particle size distribution, the instrument can count up to 3000 particles per second. Usually it is sufficient to run for 100 s for each measurement, so up to 300,000 particles can be counted in each measurement. This technique is much faster than the conventional microscope counting method. Sample preparation is also relatively simple. To prepare a sample, we filtered the pulp furnish through a 200-mesh screen in a dynamic drainage jar (DDJ) [10], diluted the filtrate, and stained it with a fluorescent dye.

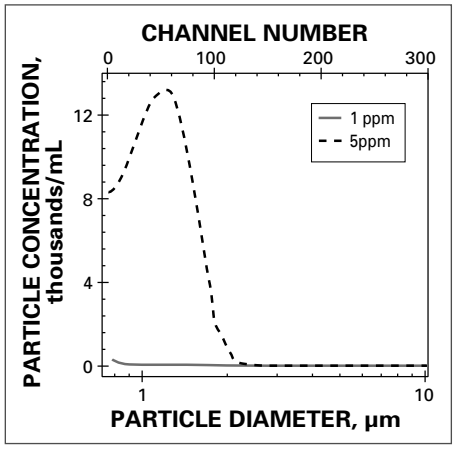
MATERIALS

Samples

For the tall oil emulsion, we diluted 1 mL of distilled tall oil with 9 mL of ethanol and mixed 1 mL of this solution with 200 mL of deionized water using a lab blender. After several hours of standing, the sample was filtered through a coarse filter paper to remove the larger



1. Diagram of the laser-optical resin particle counter.



4. The effect of a high-molecular-weight cationic copolymer on background noise.

emulsion droplets. The remaining emulsion appeared stable over a period of months in storage.

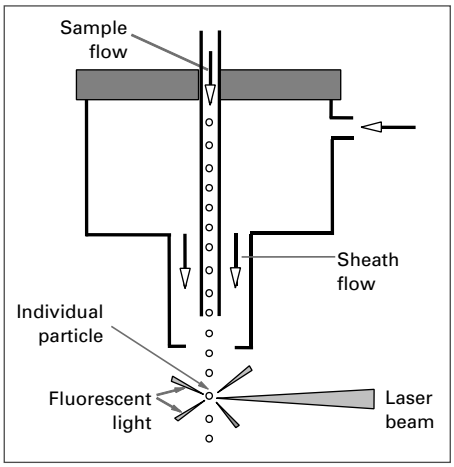
The kraft pulp filtrate was a sample of pulp machine white water from a mill producing fully bleached aspen kraft pulp. The sample was centrifuged at low speed to remove fibers and other solid materials.

TMP1 and TMP2 were samples taken from a paper machine headbox furnish in a 100% thermomechanical pulp (TMP) newsprint mill. Each was filtered through a 200-mesh screen in a DDJ.

Chemicals

The fluorescent dye was *N*-(*n*-butyl)-4-(*n*-butylamino)-naphthalimide, trade name Fluorol 7GA, purchased from Lambda Physik Inc. It has an excitation wavelength peak at 442 nm and an emission peak at 550 nm (both in ethanol).

The fluorescent latexes were purchased from Polysciences. These are polystyrene beads that are monodisperse in size and highly fluorescent. They were



2. In the flow cell of the resin particle counter, a laser beam excites individual particles stained with fluorescent dye, and the particles emit fluorescent light.

used as calibration standards for the resin particle counter.

For the polymers, we used a high-molecular-weight cationic copolymer of acrylamide and acryloyl-ethyl-trimethyl-ammonium chloride from Hercules. A low-charge cationic maize starch was supplied by Nacan.

For the fillers, the GCC powder (Omyafil) was from OMYA. It was suspended in water at 1% consistency before use. The clay sample was obtained from a TMP newsprint mill as a 59% slurry. It was also diluted to 1%.

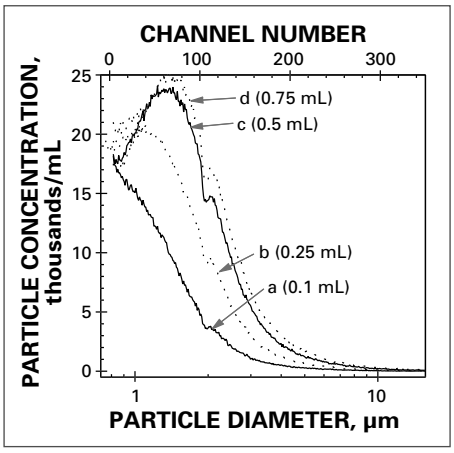
As for inorganic electrolytes, all salts were certified ACS grade from Fisher Scientific.

Pulp samples preparation

As mentioned, the pulp furnish (200–500 mL at 1% consistency) was filtered through a DDJ with a 200-mesh screen. This procedure removed long fibers and large fines. With the filtrate being stirred at 800 rpm, we collected the first 25–50 mL filtrate sample for resin particle counting.

All pulp filtrates were diluted for the particle counter. The total resin particle concentrations reported here have been corrected for dilution, so they denote the original concentration in the pulp filtrates. We estimated the particle size distribution of resin particles from the calibration curve using standard latex particles.

Unless otherwise specified, deionized water was used to dilute pulp filtrates, and doubly distilled water was used in preparing chemical solutions.



3. The effect of sample concentration on resin particle concentration. Different volumes of a TMP pulp filtrate were added to 25 mL of deionized water. Dead times and particle concentrations: (a) 13% and 1.34 × 106/mL, (b) 20% and 2.39 × 106/mL, (c) 24% and 2.90 × 106/mL, and (d) 26% and 3.14 × 106/mL.

RESULTS AND DISCUSSION

Ideal system: fluorescent latexes

Standard latexes provide the ideal system to start. They are uniform in terms of chemistry, particle size and shape, and fluorescent intensity. Typically, we would dilute a latex suspension as appropriate for hemacytometer counting and dilute the same suspension further for the resin particle counter. The measured particle concentrations for both techniques were numerically corrected for dilution so that we might report them for the same base latex suspension.

In general, agreement between the two methods was fairly good, except for the case of a 0.5 µm latex. In this case, the resin particle counter could resolve only part of the size distribution of the latex and gave a considerably lower particle concentration. The sensitivity of the instrument could be increased to cover the whole size distribution of this particular latex. With the range increased, the resin particle counter gave consistent counting compared with the hemacytometer, as in the other cases. However, for pulp filtrates, too high a sensitivity would introduce high background noise. Therefore, a balance had to be reached.

This experiment demonstrated the resin particle counter's ability to count

DILUTION LEVEL	1	0.5	0.25	0.125
Particle concentration (millions/mL)	373	284	168	95.9
Ratio*	1.00	0.76	0.45	0.26

*The ratio of particle concentration after dilution to that before dilution.

I. Effect of dilution on the resin particle concentration of a TMP filtrate

fast and accurately the particles of ideal systems (i.e., monodisperse, strongly fluorescent).

Pulp filtrate: complications

It is more complex when the resin particle counter is applied to pulp filtrates. Since the resin particles do not fluoresce themselves, a staining procedure has to be employed. The staining procedure recommended by BASF was as follows: "A pulp filtrate is diluted as necessary, usually by a factor of 100. To 25 mL of diluted pulp filtrate, add 1 mL of 40 ppm fluorescent dye in ethanol with gentle magnetic stirring. Counting starts after 2 min of mixing."

To check the validity of this procedure, we used a TMP pulp filtrate for testing. The sample was successively diluted several times to twice its volume with deionized water. The total resin particle concentration was measured for each diluted sample. The ratio of resin particle concentration after dilution to that before dilution was computed and compared with the corresponding dilution level. Ideally, the ratios should be the same as the corresponding dilution levels. The results are shown in **Table I**.

As we can see, there is a poor correlation between the resin particle concentration and the dilution level. On control samples, both the resin particle counter and a fluorescent microscope pointed up the fact that the hydrophobic dye precipitated from water and the dye particles grew with time. These fine particles were highly fluorescent and were counted as background noise. Under some circumstances, the background noise was too high, and the resin particle concentrations were unpredictable. Many other factors, such as the quality of water, the sample feed rate, the sample concentration, and the dye concentration, were also found to have significant effects on the total particle concentrations.

Figure 3 is an example of the effects of experimental conditions. In the caption, the total particle concentrations are expressed as millions of particles per mL. Conversely, the particle concentration on the *y*-axis is the count per channel in thousands of particles per mL. The "dead time" is the time when the signal analyzer is busy with signal processing and is not available for counting. Usually a high dead time is caused by a high sample feed rate and/or a high sample concentration.

Figure 3 illustrates that the right sample concentration (such that the dead time is less than 10%) is essential for a reliable measurement. It is easy to see from the caption that the total particle concentrations do not correlate with the sample concentrations. The shapes of the curves also changed with sample concentration, which should not be the case.

In Fig. 3 and in graphs of other experiments not shown, the existence of a peak in the size distribution was found to be associated with a high dead time (>10%). A high dead time probably indicates that the sample feed rate and concentration are beyond the capacity of the counter and that multiple particles

DILUTION LEVEL	1.0	0.50	0.25	0.125
Kraft pulp filtrate				
Particle conc., million/mL	231	132	81.8	42.5
Ratio*	1	0.57	0.35	0.18
TMP filtrate				
Particle conc., million/mL	460	210	116	55.9
Ratio*	1	0.46	0.25	0.12

*The ratio of resin particle concentration after dilution to that before dilution.

II. Effects of dilution on the resin particle concentration of a kraft pulp filtrate and a TMP filtrate

are passing through the laser beam simultaneously. For reliable counting, the dead time should be kept below 10%. A higher dead time was often a source of inaccuracy, as the figure shows.

Figure 4 shows the effect of a polymer (copolymer of acrylamide and acryloyl-ethyl-trimethyl-ammonium chloride) on the background noise (i.e., with no pulp filtrate added). At 1 ppm concentration, the polymer did not show any particular interaction with the dye. When the polymer concentration was increased to 5 ppm, however, the background increased sharply, indicating a strong interaction between the dye and the polymer. The exact nature of this interaction is not known at this point, but it demonstrates that a polymer can interact with the dye to interfere with the particle counting.

With the various sources of interference identified, several strategies for tackling the problem were determined. The dye precipitation in water should be kept to a minimum, the concentration of interfering materials should be kept as low as possible, and the sample concentration and feed rate should be selected to ensure a dead time of under 10%. The modified dyeing procedure is as follows: "To 25 mL of deionized water, add 0.1–0.5 mL of pulp filtrate, then 1 mL of 20 ppm dye in ethanol/DMSO (50:50) (or 100% ethanol) with gentle mixing. Discontinue mixing as soon as the dye is well mixed, and start measurements 4 min later."

In general, particle concentration tended to increase with dyeing time. Only those measurements taken between 4 min and 10 min were relatively stable. Therefore, it is important to keep the dye concentration and the dyeing time constant for all measurements. Other conditions, such as sample feed rate and sheath flow rate, must also be kept as constant as possible over different runs.

Pulp filtrate: new procedure

To test the modified procedure, two samples were chosen: the kraft and TMP pulp filtrates. As before, these samples were diluted, and the corresponding particle concentrations were compared. **Table II** lists the results, which show that the two systems responded differently to dilution. TMP was quite stable under dilution, as a result of both charge and stereochemical stabilization [11–13]. Therefore, the particle concentrations corresponded well to the dilution levels. Moreover, the data suggest that the modified dyeing procedure is working well. As for the kraft filtrate, after dilution, some coalescence of small particles may have occurred to give particles larger than 0.8 μm, which increased the particle concentration.

We also investigated the possible influences of chemicals such as multivalent ions on the background noise. **Table III**,

ION CONCENTRATION (M)	0.001	0.004	0.01
$CaCl_2$	13.2	14.2	10.5
$ZnSO_4$	9.85	9.15	10.3
$MgSO_4$	20.3	14.1	14.4
Alum (pH = 5)	12.3	14.4	18.9
Control (water)	12.8	—	—

III. Effects of multivalent ions on background counts, thousands/mL

which lists the effects of multivalent ions, shows a bit of data scattering, but note that the units are in thousands per mL, which is basically background. Apart from 0.001*M* $MgSO_4$, the rest of the data are not far from the control, which is doubly distilled water with the dye. We suspect that some materials in tapwater, multivalent ions in particular, could react with the dye. However, data in Table III did not point to any of the particular ions tested.

We also investigated the possible influences of fillers and cationic polymers on the background noise. The counts were 30,200 for filler clay and 16,100 for GCC filler, as opposed to 12,800 for the control. Consequently, both clay and GCC fillers, at typical concentrations after sample dilution, had little effect on background counts. These data indicate that the hydrophobic dye does not adsorb on hydrophilic filler surfaces. Furthermore, the scattering from the filler particles was negligible. Therefore, it is safe to use samples containing fillers.

Figure 4 shows a large increase of background counts when a cationic copolymer concentration reached 5 ppm. In **Table IV**, the same copolymer is compared with a cationic starch analyzed by the new dyeing procedure. Up to 4 ppm, both polymers showed little influence on the background. At 10 ppm, however, the background counts increased by 100-fold for the copolymer and 3-fold for the starch. In reality, it is unlikely the cationic polymer concentration will reach 4 ppm in white water. Therefore, the polymer–dye interaction can be safely ignored in most cases except where very high dosages of cationic polymers are used.

Figure 5 compares results from the resin particle counter with the results obtained with a hemacytometer for four samples. For the tall oil emulsion, which had a size distribution similar to those of the pulp filtrates but had no fines, the resin particle counter gave particle concentrations similar to those of the hemacytometer, though slightly lower.

This result demonstrates that the sensitivity of the resin particle counter is marginally less than that of the hemacytometer. The lower limit of a microscope with a 40x objective for polystyrene latex is approximately 0.5 μm. Since the refractive index of tall oil is lower than that of polystyrene, we would expect the lower limit of resolution for tall oil and resin particles to be higher. **Figure 6** shows this lower limit range as a shaded area from 0.5 μm to 0.7 μm on a distribution curve for suspended resin particle size. The laser-optical resin particle counter, on the other hand, could reliably detect only those resin particles greater than about 0.8 μm. As the figure shows, most resin particles are in the size range of 0.2–2.0 μm, peaking at roughly 0.75 μm. However, the number of particles greater than 0.8 μm accounts for most of the volume of dispersed resin, which tells us that the sensitivity of the new instrument is adequate.

There is a trend evident in Fig. 5. The ratio of particle concentration measured with the resin particle counter to that measured with the hemacytometer increases with increasing fines content. That is, the resin particle counter gave higher particle concentrations for samples with higher fines contents. This result suggests that the resin particle counter counts some fines as resin particles. However, these data alone are not conclusive because the difference could have been caused by a difference in chemical composition of the resin particles in the furnishes, which may affect the dye uptake.

POLYMER CONCENTRATION	CONTROL	1 PPM	4 PPM	10 PPM
Starch	12.8	12.5	16.6	44.1
Copolymer	12.8	12.2	14.7	1584

IV. Effects of cationic polymers on background counts, thousands/mL

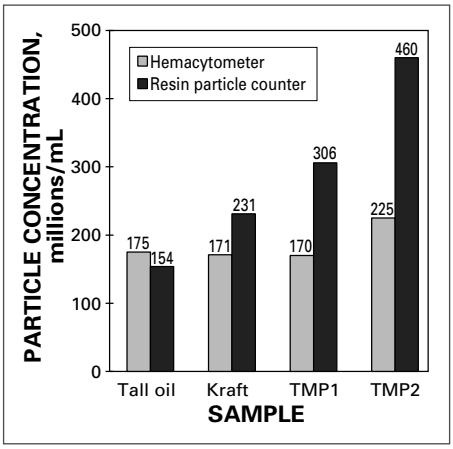
Pulp filtrate: dispersed resin in supernatant and sediment

To strengthen the conclusion that the resin particle counter does count resinous fines as well as resin particles, we conducted another set of experiments. The total number of particles in the pulp filtrates was counted as before. The same filtrate was centrifuged at 4000 rpm for 10 min, and the supernatant (containing the dispersed resin) was carefully withdrawn. The sediment (containing mostly fines) was dispersed again with distilled water by gentle shaking, and this suspension was centrifuged again under the same conditions. The process was repeated four times, after which the last supernatant looked very clear. Both the redispersed sediment and the first supernatant were analyzed with the hemacytometer and the resin particle counter.

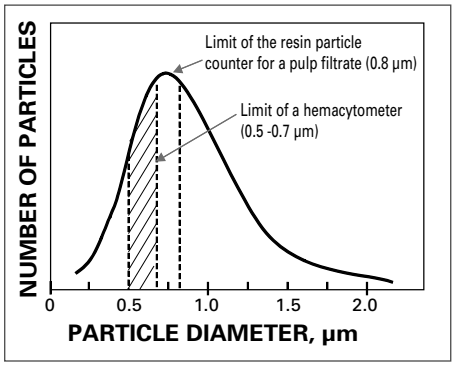
For sample TMP1 analyzed with the resin particle counter, **Fig. 7** shows that both sediment and supernatant portions contribute to total particle concentration. Microscopic observation showed fines present but no resin particles present in the sediment portions of all samples tested. Although on average the sediment particles were considerably larger than the supernatant particles (seen through a microscope), they appeared roughly the same size to the resin particle counter. This outcome indicates that it is the amount of dye sorbed by the particles, rather than the physical size, which determines the apparent resin particle size. The amounts of dye sorbed on resin particles or fines are, in turn, probably determined by the amount of extractives present. The detailed results for three different furnishes are given in **Figs. 8 and 9**.

As these graphs show, the resin particle counter cannot distinguish either kraft or TMP fines from resin particles. Fibers and fines, particularly those of mechanical pulp, have surfaces that are coated with wood extractives, and the dye will adsorb on the extractives. If the dye concentration on any of the fines is high enough, those fines will register fluorescent signals as resin particles. Although the extractives concentration on fines is lower than it is in suspended resin particles, the fines are often much larger. Hence, it is quite possible that the fines could take up the same amount of dye, or even more than the resin particles contain.

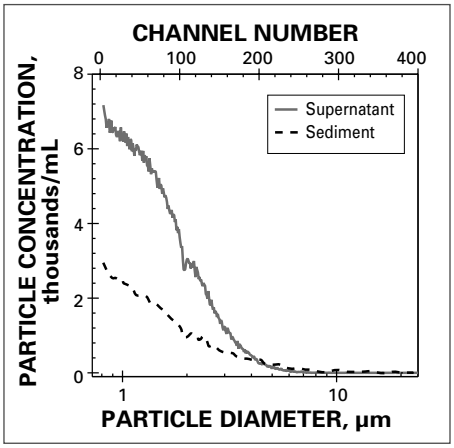
The hemacytometer results presented in Figs. 8 and 9 also reveal that the supernatant still contained fines but the sediment portion did not have resin particles. From the relative



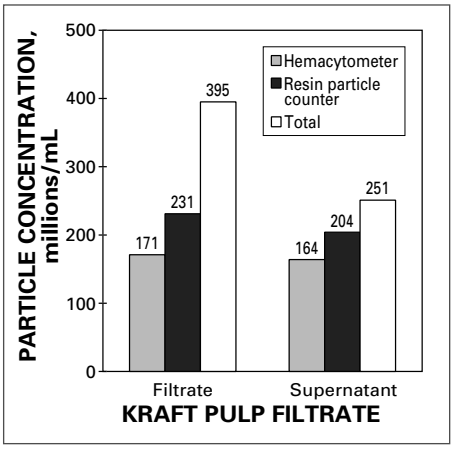
5. Comparison of results from the resin particle counter with results obtained with the hemacytometer for four samples.



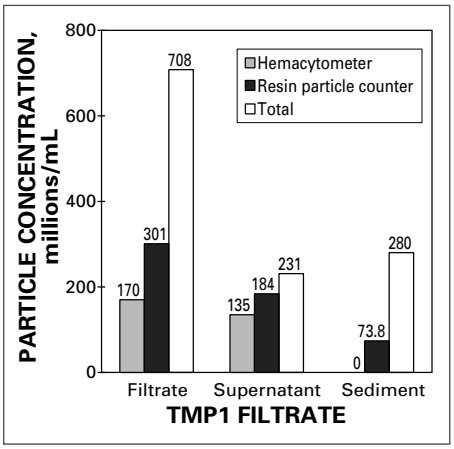
6. A representative distribution for suspended resin particle size, showing the limits of hemacytometer and the resin particle counter. The limit of the hemacytometer depends on the relative refractive index of the suspended particles and the fines content. The resin particle counter is limited by photomultiplier noise.



7. Resin particle concentration of supernatant and sediment portions of TMP1 pulp filtrate.



8. Particle concentrations in separated kraft pulp filtrate. Total particle numbers (resin particles and fines) were obtained with the hemacytometer. The sediment was flocculated and could not be redispersed.



9. Particle concentration in separated TMP1 pulp filtrate. Total particle numbers (resin particles and fines) were obtained with the hemacytometer.

resin particle concentration (determined by the resin particle counter) over the total fines (determined by the hemacytometer) in the sediment portion, it can be seen that the resin particle counter counts only about 30% of the fines in TMP filtrates. Presumably, some fines are not coated with enough wood extractives to take up enough dye to be detected by the resin particle counter.

CONCLUSIONS

The laser-optical resin particle counter is fast and efficient for well-defined monodisperse systems such as fluorescent latexes. In counting dispersed resin particles in pulp filtrates, the instrument is affected by both the sample preparation and dyeing procedure.To get reliable results from this instrument, a new dyeing procedure has been developed to minimize dye precipitation from water.

The instrument gave reproducible results for pulp filtrates once the experimental conditions, such as sample concentration, sample feed rate, and sheath flow rate, were carefully controlled so that the dead time was less than 10%. Fillers had negligible effects, but we found that high dosages of cationic polymers can interact with the dye to interfere with the resin particle counting.

The study showed that the instrument can be used as a resin particle counter, as long as it is remembered that it counts both resin particles and some fines coated with extractives. In many mill circumstances, it is probably quite appropriate to count both, because pitch deposits usually contain resinous fines. **TJ**

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INSIGHTS FROM THE AUTHORS

Pulp and paper mills worldwide have been measuring the concentration of pitch with a blood-counting chamber, or hemacytometer, and an optical microscope. BASF has developed a device that uses laser optics to measure the concentration of dispersed resin particles in pulp and paper white waters, which we evaluated in this study.

White water is treated with a fluorescent dye and fed into the particle counter. Through hydrodynamic focusing, the suspension of resin particles is caused to flow into a very narrow stream, where each particle is individually noted as it passes by a photomultiplier.

To differentiate resin from other particles in the stream, the particles are illuminated with laser light. The stained resin particles fluoresce at a different wavelength, which is picked up by the photomultiplier.

At the fluorescent dye concentrations recommended by BASF, we had difficulty with the reproducibility of results obtained with the instrument. We had to design a new dye dissolution procedure to reduce the concentration of dye. Lowering the dye concentration stopped the dyed particles from precipitating, which had been causing the reproducibility problems.

The instrument's lower limit of resolution is determined by photomultiplier noise and was found to be approximately 0.8 µm in pulp filtrates. Particles detected above this lower limit size represent the larger half of resin particles in a typical size distribution. In other words, the instrument counted only the larger half of the population of particles. With conditions carefully controlled, the instrument gave reproducible results with pulp white waters.

Staining is not entirely selective because fines, particularly mechanical pulp fines, are often coated with wood extractives. To the instrument these fines were indistinguishable from resin particles, and the counter gave a higher particle concentration than the hemacytometer gave for pulp filtrates. In pulp and paper mills, it is probably appropriate to count resinous fines, however, because they are found in pitch deposits.

The instrument we tested is a prototype. It will need modification before it can be readily used by mill personnel. In terms of assessing the instrument's performance, the next step is to look at how well it evaluates polymer flocculation and the coagulation of dispersed resin.

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