PERFORMANCE OF POLY(ETHYLENE OXIDE)/COFACTOR RETENTION AIDS IN MECHANICAL PULP FURNISHES

Gunar Laivins, Marco Polverari, and Larry Allen

Pulp and Paper Research Institute of Canada (Paprican), 570 Boulevard St. Jean,
Pointe Claire, PQ, Canada H9R 3J9

ABSTRACT

Although PEO/cofactor systems have proven to be reliable in dozens of mills, changes in the composition of furnishes (e.g., the use of deinked or peroxide-bleached pulp) have increased the need to develop novel PEO/cofactor systems. This current study examines the roles of the pulp furnish and of its white water on the performance of retention systems. The retention systems, based on combinations of PEO with each of eight commercially available cofactors, were evaluated using both laboratory-prepared and mill-generated mechanical pulp furnishes. Our findings suggest that much of the variability in the performance of a PEO/cofactor system can be eliminated by limiting or controlling variations in the ionic composition and quality of mill white water. We are now better able to suggest which PEO/cofactor combination will be best suited to a particular mill's white water, thereby eliminating performance variations.

INTRODUCTION

Although many polymers have been used as retention aids in the manufacture of newsprint and mechanical printing grades, a laboratory survey of potential retention aids for newsprint carried out some 18 years ago identified poly(ethylene oxide), PEO, as the most promising *(1)*. Over the years, PEO has proven to be a reliable retention aid in dozens of paper mills using mechanical pulp furnishes. Initially, some variability was observed in the performance of PEO in mill environments *(2, 3, 4, 5, 6)*. Much of this variability has now been tracked down and eliminated.

For example, PEO alone performs better in some newsprint mills than in others *(7)*. This variability was attributed to the presence of a second, unidentified material that is indigenous to most pulps but is not present in sufficient quantities in some *(8)*. The search to identify this PEO-performance-enhancing material led to the discovery of polymeric materials that acted as cofactors for PEO. In modern mill practice, a cofactor is mixed into a furnish prior to the addition of the PEO flocculant. Thus, PEO and a cofactor are termed a dual retention system. Such dual retention systems improve the retention and lessen the variability of the performance of PEO.

Other factors that have improved the reliability of PEO include: the development of improved makedown technologies (that ensure complete dissolution); the use of nonchlorinated water for dissolution; and the recognition that PEO is shear sensitive. The shear sensitivity dictates that PEO should be added after the fan pump and pressure screens of a paper machine, but sufficiently in advance of the headbox to ensure good mixing.

With the above improvements, PEO/cofactor systems have enjoyed good reliability. The recent trend toward greater amounts of recycled paper in newsprint has led to greater usage of retention aids because papermakers want to retain more of the clay introduced as part of the recycled furnish. Clearly, the presence of a high concentration of anionic material in the water will harm the performance of retention programs using cationic polymers such as the polyacrylamides. To overcome the impact of dissolved and colloidal substances (DCS), obvious but costly strategies are to increase the dosage of cationic polymers or to use polymers with higher positive charge densities. On the other hand, retention programs using PEO can be anticipated to perform well in white waters charged with anionic materials because PEO is nonionic and thus less affected by DCS *(7, 9, 10)*. Furthermore, reports have been published asserting that some DCS components in the white water may even improve the performance of retention systems using PEO. In line with such speculation are the observations that the retention often drops when the white water is made cleaner by replacing portions of it with fresh water *(7, 10)*. A recent Paprican study of the effects of system closure on the performance of the traditional retention and drainage aids in TMP (thermomechanical pulp) newsprint manufacture found PEO used in conjunction with a cofactor to be the retention system of choice at high degrees of closure *(11)*.

Despite the aforementioned advances in PEO technology, changes in the composition of furnishes, such as the inclusion of deinked or peroxide-bleached pulp, have increased the need to develop novel PEO/cofactor systems that are particularly suited to such furnishes. The difficulty in the development of a universal PEO retention system may emanate from the wide range of furnishes that are used in the production of newsprint and mechanical printing grades of paper.

An investigation of the effect of furnish on the performance of several PEO-based retention systems was carried out 16 years ago *(12)*. Although the study included headbox stocks from 11 different newsprint and groundwood specialty mills, the overall conclusion was that the effect of furnish composition on retention performance was not clearly understood. A clear understanding of the effect of furnish could not be found because the effect of furnish was not separated from the effects brought about by differences in the white waters. Furthermore, there is a need to re-examine this question of furnish type because of significant changes made recently in furnish compositions. For example, fewer Canadian newsprint mills are using alum, and many mills are producing mechanical printing grades of paper. Such furnishes often include bleached thermomechanical pulps, deinked pulps, and clay or calcium carbonate fillers. There is also a greater selection of cofactors available for use in conjunction with PEO *(13)*.

Although it is not our intention to examine all possible furnishes that include mechanical pulps, in this report we look at what role the furnish plays in the performance of the commercially available PEO/cofactor dual retention systems. Are the different types of fines and fillers present in a furnish responsible for the variability in performance of PEO-based retention systems? Must the PEO/cofactor retention program be tailored to the type of furnish being produced by a mill, and if so, how?

EXPERIMENTAL

Chemicals

Poly(ethylene oxide) (Floc 999) with a nominal molecular weight range of 6–9 million was obtained from E.QU.I.P. International. The PEO was used without any purification. First, a stock solution was prepared in a flask by dispersing 0.2 g of the powder in 2 mL of ethanol. This was then made up to 100 mL by adding deionized water. To ensure complete dissolution, the flask was mechanically shaken for 90 min. A further dilution (6 mL to 60 mL) was carried out, thus yielding the final PEO solution that was added to a pulp suspension.

Information about the cofactors is given in **Table I**. All cofactors were provided by E.QU.I.P. International, with the exception of PSR, which was obtained from a second supplier. The solids content of each cofactor solution was obtained by a freeze-drying procedure, as described by Allen *et al. (11)*. Solutions of the cofactors were prepared by diluting 1 g of each commercial solution to 100 mL with water. This solution was further diluted by a factor of 10 before use in retention trials.

Fresh stock solutions of PEO and of the cofactors were prepared daily.

Cofactor	Solids, %	Chemistry
Interac 1164	48.8	Bisphenol A formaldehyde resin
Interac 1168	42.0	Phenol formaldehyde resin
Interac 1169	41.8	Sodium salt of sulfonated naphthalene polymerized with formaldehyde
Interac 1175	33.0	Sodium salt of sulfonated melamine resin
Interac 1181	31.4	Mixture of resins
Interac 1186	34.6	Sulfonated phenol formaldehyde resin
Interac 1323	40.8	Mixture of resins
PSR	30.5	Phenyl sulfone resin

Table I. Description of cofactors.

Newsprint pulp (Mill A)

The major part of the investigation was carried out using pulps obtained from one integrated newsprint mill. The mill manufactures newsprint using a furnish based on 40% groundwood, 40% high-yield sulfite, and 20% deinked pulp (Furnish A). The mill produces both the groundwood and the high-yield sulfite pulps from wood chips on site and purchases the deinked pulp in wetlap form. We obtained samples of the pulps as thick stocks and collected white water coming from the wire pit of the paper machine.

Newsprint mill A typically produces its furnish by mixing or blending several pulp types together, and so fines from each pulp are present in the white water. To evaluate the performance of retention systems by pulp type, it was necessary to obtain the pulps prior to their being blended together at the proportioner. To avoid introducing fines from the blend of pulps, the white water was filtered through a filter paper (Whatman, Reeve Angel 202) to remove all solids. This fines-free filtered white water was then used to thin the consistency of each thick stock pulp to that of the mill's headbox pulp, 0.8%. In this fashion, headbox stocks were prepared using each of the thick-stock pulps and a single white water. Thus the performance of a retention system could be evaluated with the only fines present coming from the thick-stock pulp under investigation. For this set of experiments, the white water and all thick-stock pulps were obtained from Mill A. The characteristics of the pulps are summarized in **Table II**.

Pulp type	Consistency, %	Fines content[a], %	Canadian standard freeness, mL
Groundwood (Gwd)	3.93	45.6	68
High-yield sulfite (HYS)	3.37	25.8	443
Deinked (DIP)	2.53	37.6	114
40% Gwd, 40% HYS, 20% DIP[b]	0.80	Not available	53

[a] Includes P-100 fraction (fraction passing through 100-mesh screen) as determined by Bauer–McNett classification
[b] Headbox pulp produced at Mill A

Table II. Properties of pulps from Mill A.

Bleached thermomechanical pulps (Mill B)

An increasing number of papermaking mills produce mechanical printing grades of paper from furnishes containing some bleached TMP. Two additional headbox stocks were obtained from a second mill. One was used to make newsprint, and its composition was 90% hydrosulfite bleached thermomechanical pulp and 10% deinked pulp (Furnish B1). During bleaching, a hydrosulfite dosage of 1.8 kg/metric ton of pulp is applied to the TMP to obtain a final brightness of 67–68%. The second furnish was used to produce a supercalendered grade of paper, and it was based on 61% hydrogen peroxide-bleached TMP, 4% hydrosulfite TMP, 6% kraft, and 29% clay fillers (Furnish B2). This latter furnish had a brightness greater than 70%.

Quality of white water

The experiments to determine how the quality of the white water affects the performance of retention systems were carried out by altering the white water without changing the composition of the furnish. This was done by first filtering the suspension with a Büchner funnel to separate the fibers and fines from the white water. Next, a fraction of the white water was replaced by an equal amount of liquor from the flotation cell of a deinking plant, and then the fibers and fines were redispersed.

Liquor from the flotation cell of a deinking plant was chosen for this part of our study because it has the highest concentrations of deinking chemicals and because it also contains the wood components, typically hemicelluloses and lignin, that are released from the fibers during deinking. A sample of liquor from the flotation cell was obtained from the deinking plant of a member company. The recycled stock of this deinking facility is made from newspaper and old magazines in a ratio of 3:1.

Chemicals added to the repulper, on a weight basis to fibers, are silicates (1.6%), hydrogen peroxide (0.9%), and sodium hydroxide (0.8%). Following the repulping and screening, the stock enters into the flotation cell. Chemical additions to the flotation cell are a variable amount of $CaCl_2$ and soaps of fatty acids (Serfax RP 100E) (0.46%). We designed some trials to simulate the effects of carryover of liquor from a deinking facility into the white water. The carryover was simulated by replacing portions of the white water of a headbox stock with liquor from the flotation cell of a deinking facility.

CPPA standard methods were employed to characterize the white water associated with each of the three headbox furnishes and of the liquor from the flotation cell. The analytical results are given in **Table III**. Metal ion concentrations were determined by inductive coupled plasma emission spectroscopy, and anions were determined by ion chromatography *(14, 15)*. Dissolved lignin and carbohydrates were determined by UV absorption at 280 nm and by the anthrone method, respectively *(16, 17)*.

Sample	UV lignin, mg/L	Carbohydrates, mg/L	Resin / fatty acids, mg/L	Silicates, mg/L	AOX, mg/L
Furnish A	300	385	4.77	8.0	0.43
Furnish B1	280	650	1.83	11.5	0.14
Furnish B2	390	313	3.77	40.3	0.12
Flotation cell liquor	420	813	…	61.6	0.50

	ION CONTENTS, mg/L										
	Al	Fe	Ca	Mg	Mn	Na	K	$Cl^!$	SO_4^{2-}	PO_4^{2-}	CO_3^{2-}
Furnish A	1.3	0.3	8.5	1.4	0.8	72.4	17.5	7.5	116	# 1	61.8
Furnish B1	2.9	0.5	34.4	6.9	2.6	165	18.4	32.1	368	1.3	25.8
Furnish B2	1.3	0.6	19.7	5.3	1.4	458	16.9	40.3	508	3.3	128
Flotation cell liquor	1.8	0.5	124	5.8	0.5	388	16.0	338	270	1.9	31

Table III. Characterization of white waters.

Retention measurements

Measurements of first-pass retention (FPR) were made using a standard dynamic drainage jar (DDJ). This equipment was designed by Britt and Unbehend to measure fiber retention in the laboratory under shear conditions *(18, 19)*. Operating conditions were chosen to avoid the formation of a mat *(20)*. Thus, the vaned jar was fitted with a perforated stainless steel plate with mesh size 40, and the suspension was stirred at 750 rpm.

A 500-mL volume of headbox stocks or prepared stocks was poured into a beaker and heated to 60°C on a hotplate. The pH of the suspension was set to 5.2 by stirring in hydrochloric acid or sodium hydroxide as needed. Following this adjustment, an aliquot of a cofactor solution was added to the suspension, which was stirred for thirty seconds. Next, the speed of the propeller was adjusted, and the hot suspension was poured into the DDJ. The suspension was stirred for 15 seconds prior to the addition of an aliquot of PEO. The size of the aliquot was predetermined to give a dosage of 75 g per metric ton of dry pulp for all the trials. The suspension was stirred for an additional 15 seconds prior to removal of the drainage clamp at the bottom of the device. The first 25 mL of effluent were discarded and the next 100 mL were collected. This effluent was drained through a preweighed filter paper. The filter paper and contents were dried and reweighed.

The solid material suspended in the white waters of DDJ trials was quantitatively separated into the fractions of clay and of pulp fines. This was easily accomplished by filtering the white water and collecting the solids on an ashless filter paper that had been preweighed. The paper and contents were dried and then weighed. The difference in weights gave the dry weight of the solids in a sample of white water. Then the paper and contents were ashed in preweighed crucibles for four hours in an oven at 625°C. The amount of clay in the sample was obtained from difference in weights. The ratio of the weight of ash to total solids is then the fraction of clay in the white water.

FPR values were calculated according to Eq. 1, where C_s is the consistency of the stock suspension poured into the DDJ and C_{ww} is the consistency of the white water drained from the DDJ.

$$\mathrm{FPR} = \frac{(C_s - C_{ww}) \times 100}{C_s} \quad \textbf{(1)}$$

First-pass ash retention (FPAR) values were calculated for trials in which the stocks contained clay fillers. Equation 1 was modified slightly to redefine C_s and C_{ww} as the consistencies of clay fillers in the stock suspension and in the white water drained from the DDJ, respectively. The values reported are the averages of at least two trials.

RESULTS AND DISCUSSION

Effect of pulp type

An objective of this work was to examine the roles of the pulp furnish and its associated white water on the performance of dual PEO/cofactor retention systems. Therefore, as previously described, we prepared headbox stocks taking special precautions to ensure that the effect of the furnish type on retention performance was separated from the effects brought about by the composition of the white water. These precautions allow us to evaluate the performances of the retention systems with the only fines present being those produced along with the pulp under investigation. Consequently, the fines contents of the laboratory furnishes are lower than typical mill furnishes.

Figure 1 shows the change in the first-pass retention for each of the individual pulps brought about by using dual PEO retention systems. First-pass retentions were determined using PEO as the sole retention aid and then in combination with each cofactor at several concentration ratios. All experiments included a control without any retention aid. Thus, at a weight ratio of zero, two FPR values are given. The lower value is obtained by carrying out the test without any retention polymers while the higher value is that obtained when using PEO alone at a dosage level of 75 g/metric ton, without the prior addition of a cofactor. Some caution is needed when comparing the performances of the retention systems because cost is a major consideration, and the cofactor solutions have differing amounts of water and of solids (Table I). The *x*-axis gives the weight ratio of cofactor to PEO, expressed in terms of solids. Note that some of the cofactors are mixtures, and it is not known whether all components are actually active. For simplicity, we assume that all solids are active.

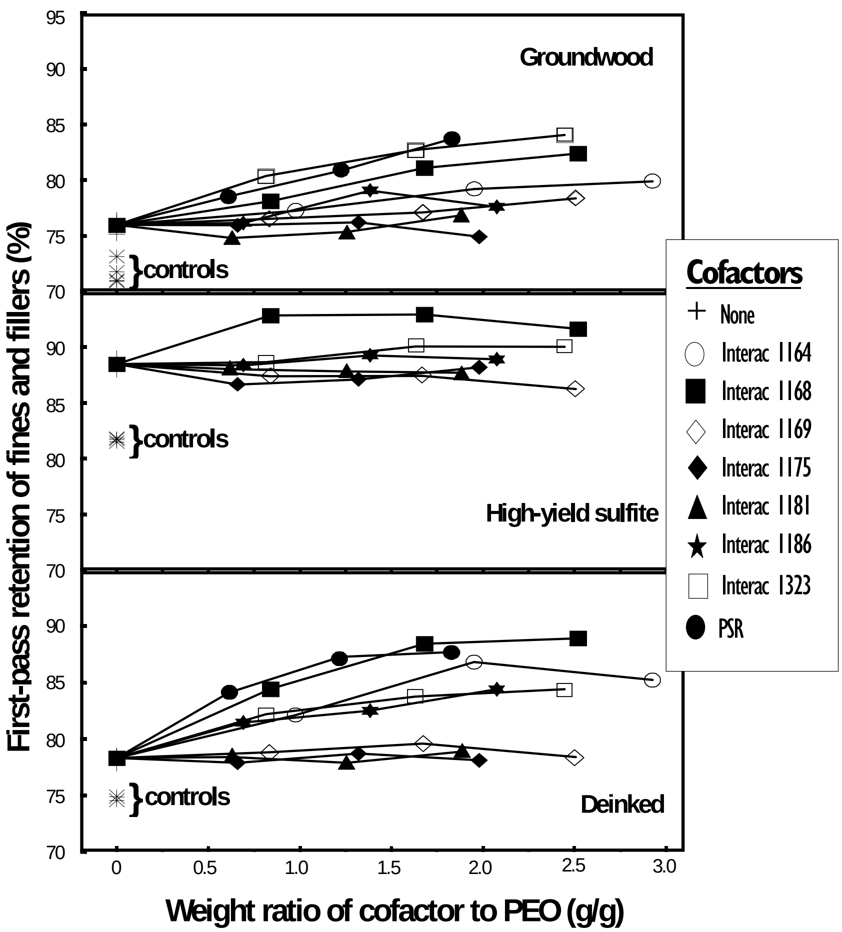

Figure 1. Retention performance of PEO/cofactor dual systems with stocks of mechanical pulp, high-yield sulfite, and deinked pulp. Control tests were carried out without addition of PEO or any cofactor.

The uppermost diagram gives the data for the groundwood pulp. The plot shows several features. First, PEO is an effective retention aid by itself, with the retention jumping by several points when using PEO at a dosage level of 75 g per metric ton of pulp. Second, when used in combination with certain cofactors, the gain in retention is even higher. Third, for some retention systems, increasing the cofactor dosage gives additional gains in the FPR. Finally and most importantly, the data clearly indicate that certain PEO/cofactor retention systems outperform others. It is this last feature that is of particular interest. The ordering of the dual retention systems in terms of performance from best to worst of the retention systems was found to be Interac 1323 > PSR ≈ Interac 1168 > Interac 1164

> Interac 1186 ≈ Interac 1169. The other two cofactors (Interac 1175 and Interac 1181) did not seem to improve the retention above that brought about by PEO only.

The middle diagram shows how the PEO-based systems perform with a high-yield sulfite pulp. While the cofactors PSR and Interac 1164 were not tested, clearly the cofactors of choice for this particular pulp are Interac 1168 followed by Interac 1323.

The lowermost diagram compares the performances of the PEO/cofactor systems using a 100% deinked pulp. This pulp was produced from old magazines and newspaper and thus contains fillers (7.7% by weight). The data for the deinked pulp are of particular interest because of reports that the inclusion of deinked pulp into a furnish adversely affects the performance of PEO-based retention programs *(13, 21)*. A most striking feature is that certain PEO/cofactor retention systems perform very well even with a stock containing only deinked pulp. The five best performing cofactors for PEO, from most to less effective, were Interac 1168, PSR, Interac 1164, Interac 1323, and Interac 1186. Although these data are most encouraging, it should be noted that this laboratory study was carried out using filtered white water, which was not recirculated. Furthermore, because the deinked pulp was purchased by the mill, it had been dried prior to shipping, thus removing the water and most of the deinking chemicals.

It is of interest to compare the performance of the retention systems with three different pulp types dispersed in the same white water. When using PEO only as the sole retention aid, at a dosage level of 75 g/metric ton, the first-pass retention values rise going from groundwood to deinked and then to the high-yield sulfite pulp. This pattern of increasing FPR values follows from the fines content of each of the pulps. The lower the amount of fines, the higher the first-pass retention. The furnish prepared from these pulps in unfiltered white water has a significantly higher fines content and a much lower first-pass retention when using PEO only. When using dual retention systems, some cofactors give an additional rise in the retention above that obtained when using PEO only. However, the ordering of the performances of the PEO/cofactor systems for the different types of pulps remains similar, suggesting that the type of fines plays only a minor role in the retention mechanism.

To further examine the role of the type of fines particle in the retention, some additional experiments were carried out. For these trials, we added clay filler to Furnish A. **Figure 2** shows the change in the retention brought about by using PEO alone and then in combination with the cofactors. A remarkable difference between this diagram and the previous one is the low first-pass retention obtained when using only PEO at a dosage level of 75 g/metric ton. The drop in the FPR is due to the high content of fines and clay in the furnish; fines and filler pass more easily through the wire mesh of the DDJ than do fibers. The additional particles come from the white water, which was not filtered, and the clay particles that were added. Once again, the cofactors that enhanced the performance of PEO were Interac 1168 > PSR > Interac 1323 > Interac 1164.

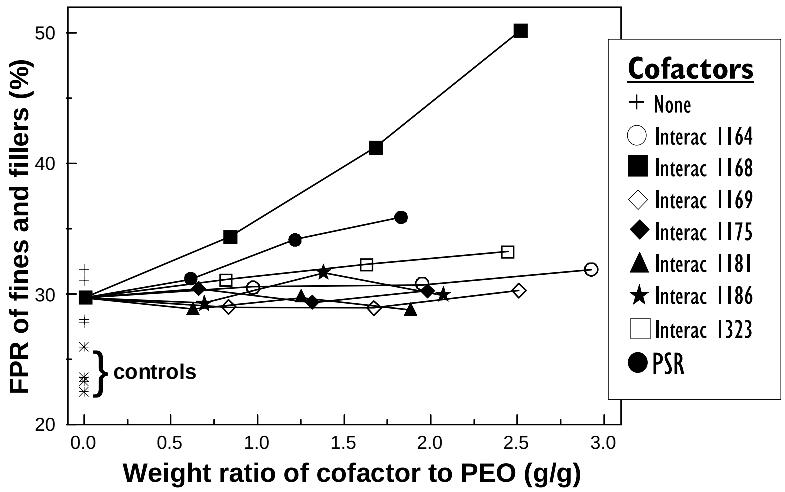

Figure 2. Changes in first-pass retention brought about by combinations of PEO and cofactors. Furnish composition: 28% mechanical pulp, 28% high-yield sulfite, 14% deinked pulp, and 30% clay.

Figure 3 gives the data for the same furnish but in terms of the first-pass ash retention (FPAR). The first-pass ash retention describes the fate of the clay particles. The control trials without the addition of any polymers give a FPAR value near to zero. This means that the concentration of clay in the white water from the DDJ is the same as that of the stock. The striking feature of this plot is that the ordering of the performances of the dual PEO/cofactor retention systems is identical to that shown in Fig. 2. This identical ordering provides additional support for the suggestion that the nature of the particle plays only a minor role in the retention mechanism.

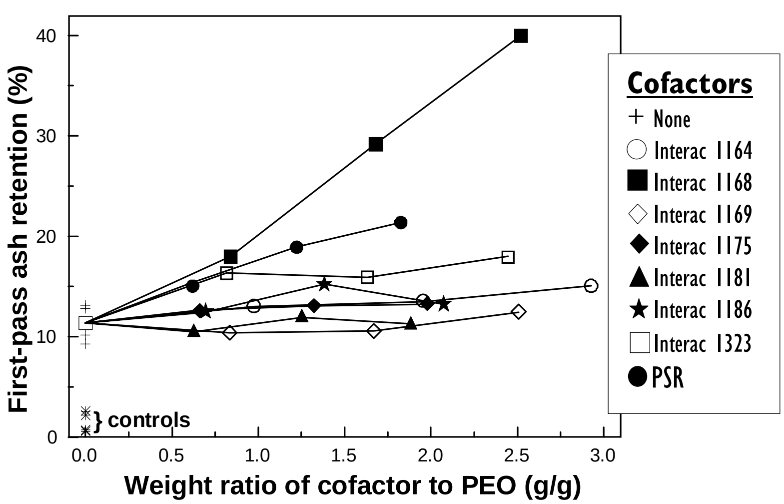

Figure 3. Changes in first-pass ash retention brought about by combinations of PEO and cofactors with stock described in Fig. 2. The ordering of the cofactors that improved the filler retention was identical to the ordering observed in Fig. 2 for overall retention.

Figure 4 shows that a linear relationship exists between the combined retention of fines and filler (FPR) and the retention of clay fillers (FPAR) no matter which cofactor is used in combination with PEO. Apparently, filler and pulp particles are similarly treated by each of the PEO/cofactor systems. If a particular PEO/cofactor system effectively retains pulp fines, then it also retains clay particles. On the other hand, dual systems that retain pulp fines poorly also are ineffective with clay particles. It follows that in order to improve filler retention, the retention of both fines and fillers must be increased. For this particular furnish, the proportionality between the FPAR and FPR is about 1.5. Thus, a gain of 1 point in the FPR will produce a gain of 1.5 points in the FPAR. While the origins for the proportionality of 1.5 are not fully understood, the properties of each type of particle present in a furnish (number, size, morphology, and surface chemistry) as well as hydrodynamic considerations (shear and turbulence) should all be considered. It is unclear how to change this proportionality without altering the furnish composition. No matter what factors contribute to the mechanism for the retention, the existence of a linear relationship suggests that the mechanism is the same for both clay filler and pulp fines.

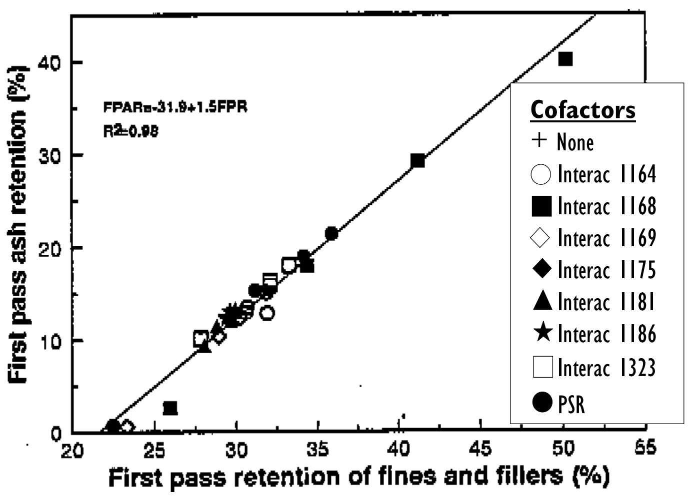

Figure 4. Linear relationship between FPAR and FPR, regardless of cofactor used with PEO. Standard error for the slope is 0.043. Furnish composition (same as in Figs. 2 and 3): 28% mechanical pulp, 28% high-yield sulfite, 14% deinked pulp, and 30% clay.

It is of some interest to examine how the retention systems affect the composition of the solids in the white waters. **Figure 5** compares the fraction of clay solids in the white water of the DDJ experiments using PEO only and then in combination with the cofactors. The clay content of the furnish was 31.1%, rising to 39.4% in the white water of DDJ trials without any retention aids. This rise indicated that the clay particles were not held up in the turbulence of the DDJ because they are larger and heavier than the fines. The data show that the solids composition of the white waters remained essentially the same for all of the cofactors. Thus both clay filler particles and pulp fines are equally retained by a particular retention system. Apparently, the PEO flocculant cannot distinguish between the different types of particles. A possible explanation is that the materials of the white waters adsorb onto all types of particles, thus coating them and rendering their surfaces virtually identical.

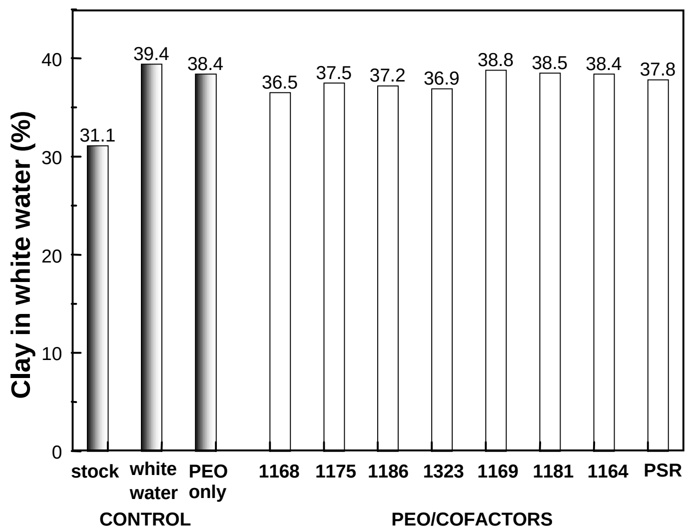

Figure 5. Compositions of the solids collected from the white water of DDJ experiments does not change appreciably as a result of using dual PEO/cofactor retention aids. Furnish composition (same as in Figs. 2–4): 28% mechanical pulp, 28% high-yield sulfite, 14% deinked pulp, and 30% clay.

Bleached thermomechanical pulp

An increasing number of mills producing newspaper and mechanical printing grades are using bleached thermomechanical pulp. Such pulps contain a high concentration of negatively charged dissolved and colloidal substances (DCS). It is anticipated that a nonionic flocculant such as PEO should perform well with bleached TMP. Our study was extended to include furnishes based on thermomechanical pulps that had been bleached to different brightness. Although both furnishes were produced at the same mill, different grades of paper were manufactured using two paper machines, each with its own white water. Some of the characteristics of the white water of Furnishes B1 and B2 are shown in Table III.

Figure 6 shows the change in the FPR brought about by the dual retention systems for the newsprint-grade furnish based on hydrosulfite TMP (Furnish B1). Despite containing 10% deinked pulp, this particular furnish clearly responds well to PEO-based retention systems. It is difficult to rank the cofactors according to their performance. At low dosage of cofactor, the combination of PEO and PSR clearly excels. On the other hand, the combination of Interac 1323 and PEO gives a smaller initial response, yet the FPR steadily improves with larger cofactor dosages. Clearly, the combination of PEO and Interac 1323 has not yet attained its upper limit of performance. Other cofactors giving good results are Interac 1164 > Interac 1168 > Interac 1186.

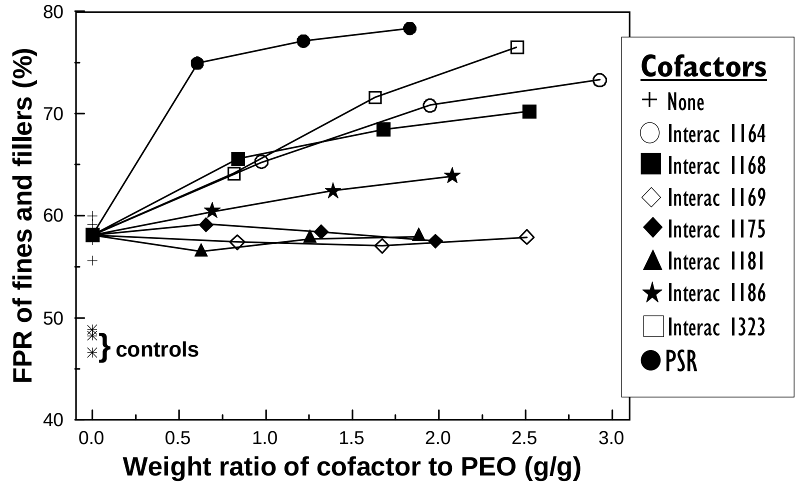

Figure 6. Effect of dual PEO/cofactor retention aids on FPR of a low-brightness TMP. Furnish composition: 90% hydrosulfite TMP and 10% deinked pulp.

Figure 7 gives the data for Furnish B2 based on the hydrogen peroxide-bleached TMP. An interesting observation is the large jump in the FPR brought about by using PEO only. However, the error associated with these replicates also is quite high. Thus, our first conclusion is that PEO is an effective retention aid for peroxide-bleached TMP, and because it is so very effective, we speculate that the stock contains a substance that can function as a cofactor for the PEO flocculant. The drop in the retention when PEO is used in combination with two of the cofactors (Interac 1168 and Interac 1175) may indicate that these cofactors hinder the interaction of PEO and the cofactor-like substance. It is noteworthy that the individual components of 1323 perform poorly while 1323, a mixture of the components, shows a positive effect. The cofactors of choice for this pulp are PSR > Interac 1164 > Interac 1323.

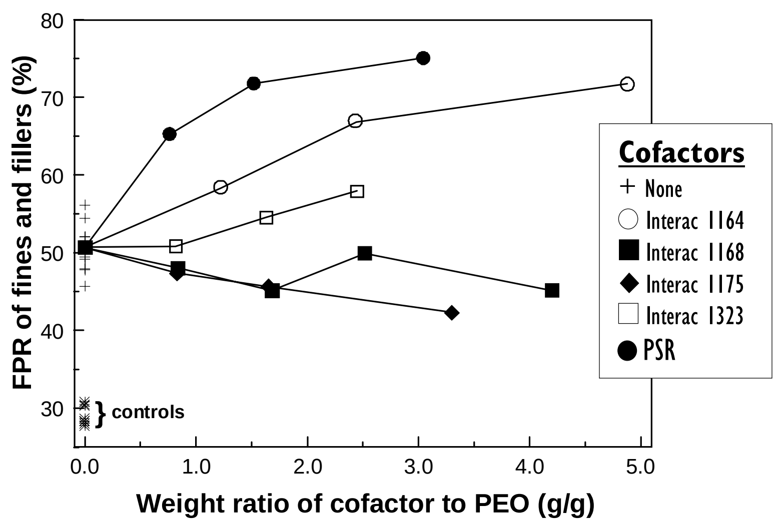

Figure 7. Effect of dual PEO/cofactor retention aids on FPR of a high-brightness TMP. Furnish composition: 61% hydrogen peroxide-bleached TMP, 4% hydrosulfite TMP, 6% kraft, and 29% clay fillers.

Figure 8 shows that a linear relationship exists between the FPAR and FPR for furnish B2. Once again, this indicates that the PEO flocculant cannot distinguish between particles of clay filler and pulp fines. The proportionality between the filler and total retention is 1.38. This value is rather close to the proportionality of 1.5 obtained for the data of Fig. 4. Perhaps this is not unexpected, since both furnishes have similar filler contents. Apparently, the type of clay also is not too crucial.

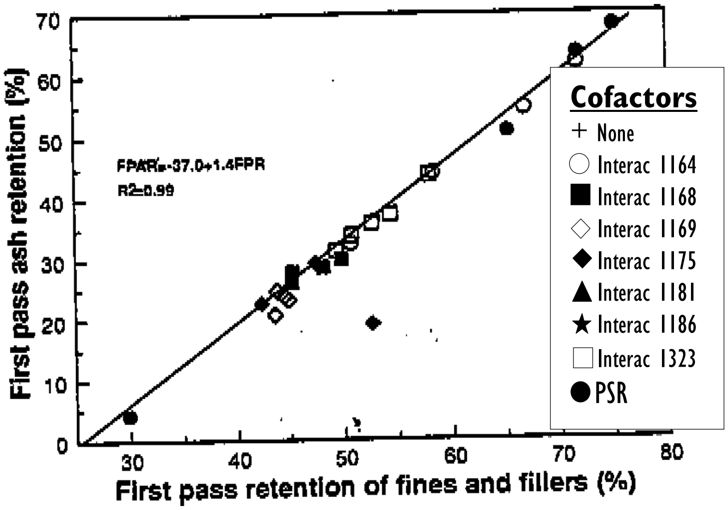

Figure 8. Correlation between FPAR and FPR for Furnish B2 shows that FPAR increases with increasing FPR. Standard error for the slope is 0.024.

Effect of white-water quality

Our finding that all of the dual PEO/cofactor systems are nonselective towards the retention of clay fillers or of pulp fines — coupled with the observation that the type of pulp plays only a minor role in the retention mechanism — points to the white water as having a predominant effect on the performance of the PEO retention systems.

As discussed previously, furnishes containing deinked pulp are of special interest. Figure 1 shows that certain dual PEO retention systems work well using a stock prepared from deinked pulp only. However, because the mill purchased the pulp in drylap form, most of the deinking chemicals had been removed prior to the drying and shipping of the pulp. On the other hand, some mills have a de-inking plant on site and then produce paper using the deinked pulp without first drying it. In such cases, more deinking liquor may be carried along with the pulp into the papermaking process. The carryover was simulated by replacing portions of the white water of a headbox stock with liquor from the flotation cell of a deinking facility.

Figure 9 compares the retention response to dual PEO/cofactor systems for a hydrosulfite TMP in its white water and with 20% replacement of white water by deinking liquor. The findings show that the carryover of deinking liquor into the papermaking stage does not diminish retention when using only PEO. Next, we see that the curves connecting the filled symbols (no deinking liquor) lie above those connecting the open symbols (20% deinking liquor), indicating that the gains in retention brought about by the cofactors are significantly reduced by the deinking liquors. This suggests that a chemical in the deinking liquor renders the cofactor inert but does not affect PEO. However, the results also suggest that deactivation of the cofactor can be overcome by increasing its concentration (see Fig. 9 showing FPR for Interac 1168 at highest experimental dosage of 3.2:1). These findings are in agreement with previously reported results for a deinked pulp using a PEO/phenol formaldehyde resin (PFR) retention system *(21)*. Despite the similar findings, an important difference between the two studies is the deinking agent. Their deinking agent was an alkyloxylated surfactant, while ours was a fatty acid soap. Stack *et al. (21)* found that the alkyloxylated surfactant forms an insoluble complex with the phenolic resin and thus is unavailable for interaction with PEO. Perhaps most surprising is their finding that all surfactants did not behave similarly. In particular, fatty acid-type surfactants were found not to interfere with the retention system.

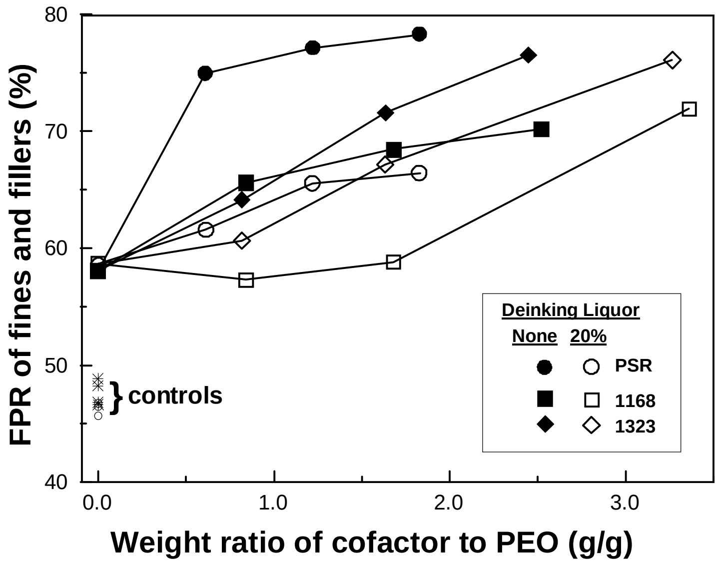

Figure 9. Effect of deinking liquor on FPR of a stock consisting of 90% hydrosulfite TMP and 10% deinked pulp. The deinking liquor diminishes the retention improvement brought about by the cofactor but does not affect the performance of the PEO.

Thus, our deinking liquor must also contain some substance other than the fatty acid soap that interferes with the cofactors, making them unavailable for interaction with PEO. Table III lists the concentrations for some of the materials in the deinking liquor. The data show that the deinking liquor is richer than many white waters in soluble lignin, carbohydrates, silicates, and adsorbable organic halides (AOX). While any of these substances are potential contaminants for the PEO retention systems, the deinking liquor also typically has high concentrations of metal ions: Chemical analysis of the deinking liquor indicated that the concentrations of Na^+ and Ca^{2+} were 388 and 124 ppm, respectively, as compared with 165 for Na^+ and 34 ppm for Ca^{2+} in the white water. Thus in our experiments, the concentrations of sodium and calcium rose to 210 and 52 ppm, respectively, due to the replacement of 20% of the white water with deinking liquor.

It is possible that the concentrations of the metal ions could play an important role in the solubility of the cofactors. A cofactor that has precipitated from solution would not be available to interact with PEO and to form a complex with PEO. The formation of a complex is thought to play an important role in the retention mechanism by which the two polymers improve retention in the papermaking process *(22, 23, 24, 25, 26, 27)*. Pertinent to this discussion are the findings that the solubility of phenol formaldehyde resin is very sensitive to the combination of pH and ionic strength. Precipitation of phenol formaldehyde resin can be achieved by lowering the pH and by increasing salt concentrations *(22, 28)*.

Figure 10 shows that the improvements in first-pass retention brought about by Interac 1168, Interac 1323, and PSR are gradually lost with a progressive rise in the concentration of the calcium ion. The natural concentration of Ca^{2+} in the furnish was 35 ppm and this was increased by additions of calcium nitrate salt to the furnish. This work shows that high concentrations of Ca^{2+} and possibly other metal ions reduce the performance of certain dual PEO/cofactor retention systems. Preliminary tests on the solubility of the cofactors showed that all were sensitive to the concentration of calcium ions. Because deinking liquor contains many substances, it is possible that part of the reduction in the retention is due to interference by a contaminant in addition to the metal ions.

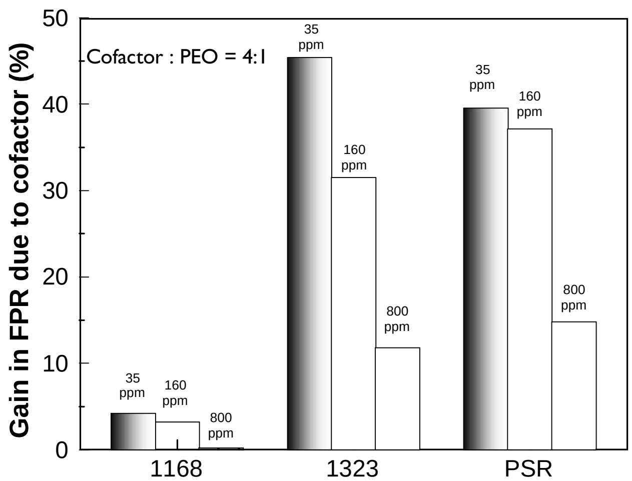

Figure 10. Effect of Ca^{2+} ion concentration (in white water) on the gain in FPR for three cofactors (Interac 1168, Interac 1323, and PSR). Tests were carried out using a cofactor:PEO dosage of 4:1 in a stock consisting of 90% hydrosulfite TMP and 10% deinked pulp.

CONCLUDING REMARKS

We have found that combinations of PEO and cofactors perform well with a number of mechanical pulp furnishes used to produce standard newsprint or mechanical printing grades. While this does not imply that a particular PEO/cofactor combination performed well with every furnish, good retention of both fines and fillers can be obtained with the correct choice of cofactor. Thus, retention aid technology based on PEO continues to be a viable option for most mills producing mechanical pulp furnishes.

In this work, the performances of several PEO/cofactor systems were evaluated solely in terms of retention. However, in practice, the PEO/cofactor system of choice is not necessarily the one that gives the highest retention. For example, too high a retention of fines and fillers during sheet formation may slow the drainage rate and lead to runnability problems. Other considerations in the selection of a cofactor include control of pitch deposition, turbidity of the effluent, and cost.

Our work examined the individual roles of the pulp furnish and of the associated white water on the performance of PEO-based retention systems. When the contribution of the white water was separated from that of the furnish, our findings showed that the order of the performance of the retention systems was insensitive to the type of mechanical pulp. Furthermore, the addition of clay to a newsprint furnish did not affect the ordering of the performances of the retention systems. This constancy in the ordering of the retention systems suggests an inability to discriminate between pulp fines or clay particles based on differences in surface chemistries. Initially, this is surprising because clay particles have very different surface chemistries from pulp fines when suspended in water. However, when suspended in a mill white water, differences in the surfaces chemistries would disappear if dissolved and colloidal substances of the white water adsorbed onto the fines and clay particles *(29)*. While the furnish composition plays only a minor role in the performance of the retention systems, the quality of the white water has a large impact on performance. For example, when the white water was contaminated with deinking liquor from the flotation cell of a deinking plant, the gains in retention for some of the cofactors were reduced significantly.

PEO has recently been shown to operate by a bridging mechanism, and the formation of a complex between PEO and a cofactor is thought to play an important role in the retention mechanism *(27)*. Our work suggests that the variability in the performance of a PEO/cofactor system is brought about by changes in the ionic composition and quality of a mill's white water. We speculate that changes in the quality and ionic contents of white water affect the solubility of the cofactors. A cofactor that has precipitated from solution is no longer able to interact and form a complex with PEO. Studies are currently under way to examine how the performances of the retention systems correlate to the solution properties of the cofactors.

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