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# New Information on the role of cofactor in PEO-type retention aid systems

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## ABSTRACT

The flocculation of three colloidal dispersions (precipitated calcium carbonate (PCC), $TiO_2$ and a calcined clay) using a combination of polymeric flocculants and cofactors was investigated. The flocculants used were PEO (MW = $9 \times 10^6$), CPAM (a cationic copolymer of acrylamide) and POLYPAM-CO-PEG (a non-ionic comb copolymer (MW = $5 \times 10^6$) consisting of a polyacrylamide backbone with ~ 1mole % pendent PEG chains). The cofactors were based on poly(vinyl phenol-co-sodium acrylate) and poly(vinyl phenol-co-sodium styrene sulfonic acid). The amount of flocculation induced was dependent on the components present in each system. Cofactors containing sulfonic acid were more calcium ion tolerant than the cofactors containing carboxyl groups. These latter cofactors formed a precipitate when exposed to $\geq$ 0.6 mM $Ca^{++}$. Maximum flocculation of PCC was obtained by using POLYPAM-CO-PEG with a cofactor containing 23 mole % of sulfonated groups. $TiO_2$ was not flocculated when PEO was employed due to the adsorbed layer thickness of this flocculant being approximately equal to half the Debye screening length in 0.001 M NaCl. However, $TiO_2$ was flocculated by POLYPAM-CO-PEG and CPAM, the best flocculation being obtained when POLYPAM-CO-PEG was used with either a cofactor containing 19 mole % sulfonated groups, or a cofactor containing 14 mole % acrylic acid groups. Overall, the easiest colloid to flocculate was the calcined clay; maximum flocculation being obtained when PEO was combined with a cofactor containing 19 mole % sulfonated groups.

In general, the flocculation was most sensitive to the charge of the cofactors. It is proposed that the hydrophobic character of the vinyl phenol based cofactor is important. Hydrophobic interaction may be a part of the cofactor interaction with PEO and subsequent complex adsorption on surfaces.

## 1. INTRODUCTION

Originally developed for filled, fine papers where the economic incentives were great, retention aid technology is now employed in all types of paper and paperboard manufacture. The newsprint industry was one of the last sectors to embrace the use of polymers(1). This was driven by the increasing use of deinked pulp, fillers and tighter white water systems. Canadian newsprint mills routinely spend millions of dollars annually on wet-end chemicals to increase machine efficiency.

Research conducted in the seventies showed that the large fluid mechanical forces in high speed newsprint machines coupled with high concentrations of dissolved and colloidal substances (DISCO) rendered cationic flocculants ineffective in newsprint(2). More recently Holmbom's group(3) and others(4,5) have started to elucidate the structures of the most troublesome DISCO components.

Currently in Canada three polymer systems are employed in newsprint manufacture. These are (not in order of importance):
1) a relatively inexpensive low molecular weight cationic followed by a high molecular weight flocculant:
2) bentonite together with a high molecular weight, low charge polyacrylamide(6); and,
3) polyethylene oxide (PEO) with a phenolic cofactor.

This work focuses on the PEO system which was first patented by the Nalco Chemical Company in 1964(7). The patent included two examples using fine paper stocks and one using mechanical pulps. However, PEO alone was of limited effectiveness and thus rarely used.

The breakthrough came with the recognition that PEO was much more effective in the presence of water borne phenolic polymers. The early patents were European(8) or were for waste water treatment(9); the potential for PEO/phenolic flocculants as newsprint retention aids went unnoticed in Canada until Pelton et al. published a comparative study which showed PEO to be most promising(10).

Mill trials in the early eighties(11) lead to the ongoing use of PEO on a few Canadian machines. In a few cases, PEO alone is effective, however, it is generally added after a phenolic cofactor. Water borne resins based on formaldehyde and phenolics are the most commercially significant cofactors, however, other effective materials include sulfonated kraft lignin(12) and poly(vinyl phenol). The retention mechanism for the cofactor/PEO system has been addressed by a number of authors(13-17) and will not be discussed herein. However, every mechanism postulated requires that aqueous PEO form a complex with cofactor. From the beginning it was assumed that the PEO/cofactor complex was based on hydrogen bond formation between the phenolic hydroxyl groups and the polyether oxygen. Stack and coworkers(18) were the first to apply molecular mechanics modeling to show that the hydrogen bonding structures shown in Figure 1 are at least geometrically possible.

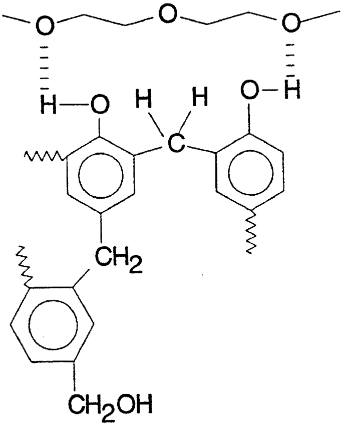


Figure 1 Possible sites for hydrogen bonding in PEO-cofactor complexes (from ref 18).

More recently Pelton et al.(19) used molecular mechanics modeling to study the interaction of polyethylene oxide with poly(vinyl phenol). The calculations indicated that only every fourth or fifth polyether oxygen participated in hydrogen bonding. This is in stark contrast to the 'zipper' model in which every ether oxygen binds to poly(acrylic acid) in a highly cooperative process(20).

There is much circumstantial evidence for hydrogen bonding. Perhaps the most significant is that under pH conditions where phenolic groups are dissociated, there is no evidence of PEO/phenolic complex formation.

In this work, it will be shown that phenolic polymers which are effective cofactors, do not interact with PEO if the phenolic hydroxyl groups are converted to esters. Nevertheless, it is puzzling that other polymers such as poly(acrylic acid) and poly(methacrylic acid), known to form hydrogen bonding complexes with PEO(20), are completely ineffective as cofactors(20). Indeed, every effective cofactor contains phenolic or other aromatic hydroxyl groups - we wished to investigate the role of phenolic groups.

Several papers on the role of cofactors have been published. Stack and coworkers(21), using a characterized series of novolac and resole resins, measured the quantity of macroscopic (i.e. did not pass through a 78 $\mu$m screen) PEO/cofactor complex as a function of pH and ionic strength. They showed that phenolics with MW < 3000 did not form a macroscopic precipitate. Both types of phenolic resin could form complexes with PEO and they postulated the interesting possibility of hydrophobic association, in addition to H bonding, between PEO and phenolic resin.

Parallel studies at McMaster and van de Ven's group at McGill(22) have revealed two fundamentally different types of cofactor behaviors. In one case, typical of the earliest phenolic resins, the interaction of aqueous PEO with the cofactor in the absence of other materials gave a polymer/polymer complex that phase separated to give a colloidal suspension or a precipitate. In the other case, the PEO/cofactor complex remained water soluble; presumably cofactors of this type are more hydrophilic. Subsequent dynamic light scattering studies at McGill revealed that when PEO forms a soluble complex, the configuration is expanded relative to uncomplexed PEO(23).

Although there have been a number of patents describing new cofactors(24), there is little published information on the role of cofactor structure in the PEO retention system. Indeed, no one has been able to capture cofactor/PEO H bonding by direct spectroscopic measurement.

Part of the experimental difficulty arises from the complicated structure of most cofactors which are made by condensation chemistry. In an effort to work with better defined polymers, we started to work with linear poly(vinyl phenol) as this polymer is an effective retention aid(19, 25).

However, linear poly(vinyl phenol) is not a good model because it is present in pulp systems as insoluble colloidal particles.

This work describes the synthesis of six model cofactors based on poly(vinyl phenol-co-sodium acrylate, SA) and poly(vinyl phenol-co-sodium styrene sulfonic acid, SSS), whose structures are shown in Figure 2.

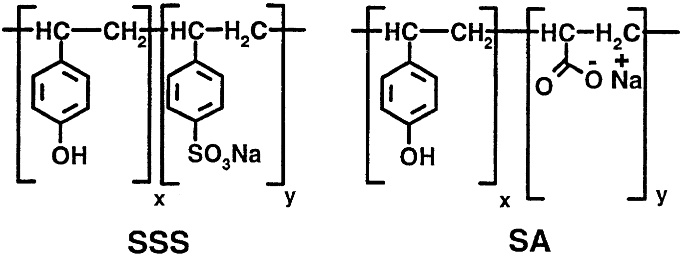


Figure 2 Structures of vinyl phenol copolymers which were evaluated as PEO cofactors.

Each cofactor was evaluated in conjunction with three flocculants, PEO, CPAM (a commercial cationic polyacrylamide copolymer), and POLYPAM-CO-PEG (an experimental flocculant consisting of polyacrylamide backbone bearing short polyethylene glycol pendent chains). Each cofactor/flocculant pair was evaluated as a flocculant for aqueous suspensions of precipitated calcium carbonate (PCC), clay, and titanium dioxide ($TiO_2$). Based on this work, preliminary conclusions are made about the role of cofactor structure in flocculation. Continuing studies are focused on characterizing the hydrogen bond complex.

## 2. EXPERIMENTAL

### Materials

The monomer 4-acetoxystyrene (ACS) and the sodium salt of 4-styrene sulfonic acid (SSS) were used as received from PolySciences. Acrylamide was obtained from Aldrich; and VAZO-64 (2,2'-azobis (2-methyl propanenitrile) from Du Pont) was chosen as an initiator. Reagent grade dimethyl sulfoxide (DMSO, from Caledon) was used as the solvent in the solution polymerization.

## Synthesis of the cofactors

Two types of cofactors were prepared. **SSS-x** type were copolymers of vinyl phenol and sodium styrene sulfonic acid where **x** is the mole percent of sulfonic acid groups. The **SA-x** type were copolymers of vinyl phenol and sodium acrylate, resulting from the hydrolysis of acrylamide, where x is the mole percent of acrylate groups. Vinyl phenol will not undergo free radical polymerization so the copolymers were prepared by free radical polymerization of acetoxystyrene with p-styrene sulfonic acid or acrylamide. A post polymerization hydrolysis step yielded the desired copolymers (see Figure 3).

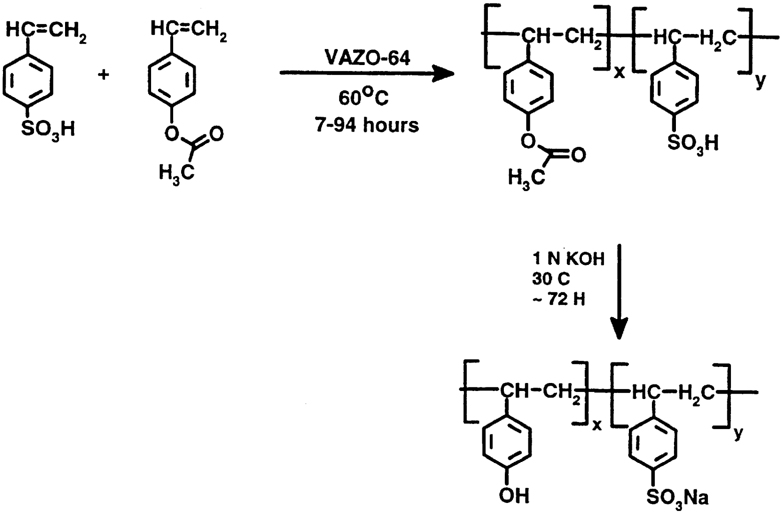


Figure 3 Synthesis of SSS cofactors.

The monomers, solvent, and initiator (for details see Table 1) were placed in a three-necked round bottomed flask (100ml) which was partially immersed in a paraffin heated bath. The contents were purged with ultra pure nitrogen and the temperature of the reactants gradually increased to 60°C. Polymerization was maintained at this temperature for 24 hours.

Table 1 Recipes and operating conditions for cofactor copolymerization

| **Name** | **ACS (g)** | **SSS (g)** | **SA (g)** | **VAZO-64 (mg)** | **DMSO (g)** | **TIME (h) (yield (%)** |
|---|---|---|---|---|---|---|
| SA-10 | 3.1 | - | 0.157 | 30.3 | 7.24 | 26<br>(~100) |
| SA-14 | 9.9 | - | 2.56 | 93 | 30.64 | 72<br>(~95) |
| SSS-16 | 6.981 | 3.008 | - | 87.3 | 19.6 | 20<br>(~100) |
| SSS-19 | 2.81 | 0.401 | - | 69.2 | 6.03 | 7<br>(~100) |
| SSS-23 | 7.83 | 5.6 | - | 208 | 31.5 | 94<br>(~100) |
| SSS-39 | 4.41 | 9.94 | - | 163 | 63 | 90<br>(~100) |

At the termination of polymerization, the products were precipitated with either acetone (in the case of the acrylate cofactors and the sulfonate cofactors with an SSS content $\geq$ 23 mole %) or ice water (in the case of an SSS content < 23 mole %). The precipitates were dried at ambient temperatures overnight and trace amounts of the dried products were collected for characterization.

The remaining solid was re-dispersed in 1 N KOH, with 6 to 8 times more base present than cofactor. The hydrolysis was conducted under a nitrogen atmosphere at 25°C for over 48 hours. The reaction conditions are shown in Table 2. The final products were precipitated with acetone and dried at room temperature.

Table 2 Recipes and conditions for the hydrolysis of cofactors

| **Name** | **KOH (1N)** | **$H_2O$ (mL)** | **Polym. Wt (g)** | **Temp (°C)** | **Hydrolysis time (h)** |
|---|---|---|---|---|---|
| SA-10 | 45 | 5 | 3.5 | 35 | 70 |
| SA-14 | 100 | 0 | 8.1 | 35 - 40 | 72 |
| SSS-16 | 30 | 15 | 2.95 | 35 | 48 |
| SSS-19 | 30 | 5 | 2.45 | 25-30 | 88 |
| SSS-23 | 60 | 0 | 4.42 | 40 | 72 |
| SSS-39 | 100 | 0 | 7.31 | 40 | 68 |

All cofactors were then dissolved in water, ion exchange beads (AG 1-X8 anion exchange and AG 50W-X8 cation exchange resin - Bio-Rad) added to the solution and the mixture stirred for 10 hours. Proton NMR traces of a sulfonated cofactor showed that after purification the solvent was completely removed and the acetic acid component, although not totally removed, was considerably reduced. The ion exchange beads were removed and the cofactor allowed to dry in air. All cofactors were stored as solid samples and dispersed in water for use.

## Characterization of the cofactors

The charge density of each cofactor was determined using a Charge Analyzer II (Rank Brothers) equipped with a streaming current cell. The sulfonic or carboxyl group content was measured by titration with 0.001 N hexadimethrine bromide (Polybrene) standard cationic solution. The molecular weight of each cofactor was around 1,000.

## Polymeric flocculants

The cofactors synthesized in this laboratory formed one part of a dual-component system. The second component was either POLYOX 309 (PEO) which is $9\times10^6$ molecular weight PEO supplied by Union Carbide: Percol-445 (CPAM), a cationic copolymer of acrylamide supplied by Allied Colloids; or a non-ionic comb copolymer (MW = $5\times10^6$) consisting of a polyacrylamide backbone with ~ 1 mole % pendent PEG chains(26) (POLYPAM-CO-PEG). The effect of these three flocculants in combination with the cofactors was tested on three different colloidal particles:

1) precipitated calcium carbonate (PCC) (Albacar HO, scalenohedral external crystal habit, mean particle size of 1.34 microns, supplied by SMI Inc.):

2) $TiO_2$ (anatase, mean particle size 210 nm, supplied by Aldrich); and

3) Hycal clay (a calcined kaolinite, with a particle size distribution of 86 - 92% finer than 2 mm, supplied by Hüber).

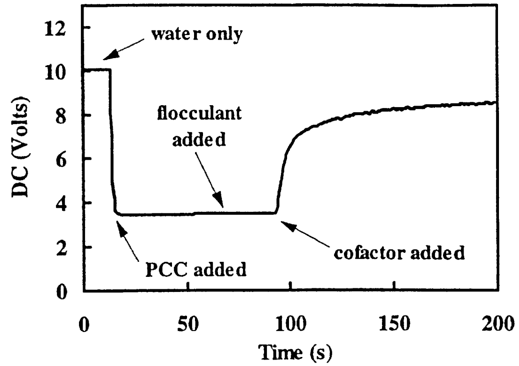


Figure 4 Typical trace obtained from the Photometric Dispersion Analyzer. Distilled water gave a voltage of 10. The addition of PCC to the system decreased this voltage. Addition of the second polymeric component allowed flocculation to occur which is shown by an increase in voltage.

## Flocculation

The ability of the polymers to flocculate the various colloids was ascertained using the Photometric Dispersion Analyzer(27) to monitor the extent of flocculation. The solutions for all experiments were made with 0.001 M NaCl and the pH values were maintained at pH 7.5. The colloidal suspension (250 ml) was placed in a 400 ml beaker and stirred at 400 RPM with a three-bladed propeller (55 mm diameter) with the suspension being circulated through the PDA at 45 ml min-1 using a peristaltic pump. After 60 seconds the first polymeric component of the flocculant system was added. The second component was then added approximately 20 seconds after the first.

Figure 4 shows a typical DC output voltage trace from the PDA.

The presence of colloidal PCC lowered the intensity of transmitted light. The flocculant (POLYPAM-CO-PEG) had no effect on the intensity of light transmission, whereas subsequent cofactor addition resulted in an increase due to the aggregation of PCC. The suspension turbidity values were calculated as $\ln(V_0/V)$ where $V_0$ was the voltage signal for water and V for the colloidal dispersion. Based on the assumption that the turbidity was proportional to the concentration of un-flocculated colloidal particles (N), the raw data was converted to a plot of $N/N_0$ versus time where $N_0$ was the initial colloidal particle concentration.

Figure 5 shows the converted data from Figure 4. These curves are approximate because it is assumed that the flocs do not contribute to the turbidity.

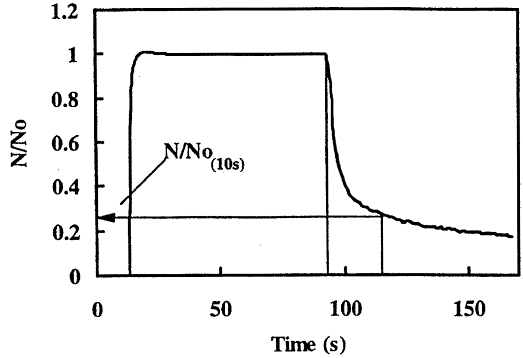


Figure 5 The PDA data from figure 4 converted to turbidity ($N/N_0$) to allow the amount of flocculation induced to be obtained.

$N/N_0$ values 10 s after the start of flocculation were recorded in order to describe flocculation curves as a single number. This parameter is illustrated in Figure 4.

## 3. RESULTS

Two poly(vinyl phenol-co-acrylic acid) copolymers, SA-10 and SA-14, were prepared and the charge content was measured by colloid titration. Similarly, four poly(vinyl phenol-co-sodium styrene sulfonic acid) copolymers, SSS-16, SSS-19, SSS-23, and SSS-39, were characterized by colloid titration and NMR.

The 6 experimental cofactors were evaluated as flocculants for PCC, clay and $TiO_2$ when used in conjunction with PEO, CPAM or POLYAM-CO-PEG. In the following sections the results are divided first in terms or the type of colloid and secondly in terms of the flocculant used with the cofactor.

## PCC Flocculation

PCC was dispersed in water at pH 7.5 in the presence of 0.001 M NaCl. Under these conditions, PCC has an electrophoretic mobility of about $+10^{-8}$ $m^2V^{-1}s^{-1}$ indicating a positive surface charge reflecting a surface excess of calcium ions. The concentration of PCC used in these experiments was 1000 ppm.

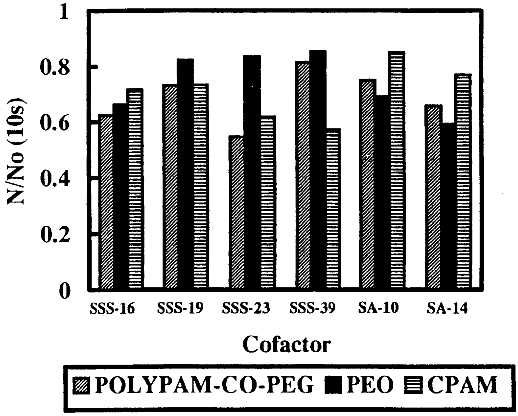


Figure 6 Flocculation results obtained for PCC. The smaller N/N$_{0(10s)}$ the more efficient the flocculation. The cofactor (2 ppm) was added before flocculant (2 ppm) addition

### a) POLYPAM-CO-PEG

POLYPAM-CO-PEG is an experimental flocculant consisting of a polyacrylamide backbone supporting pendent polyethylene glycol chains. The use of POLYPAM-CO-PEG for flocculation of latex(28) and newsprint pulp(29) has been described elsewhere. The six cofactors were used in conjunction with POLYPAM-CO-PEG to flocculate PCC and the results are summarized in Figure 6.

The lower the $N/N_{010s}$ value, the better the flocculation. Neither POLYPAM-CO-PEG nor the cofactor alone caused flocculation of PCC. When both components were used, the SSS cofactors proved, in general, to be more effective at flocculating PCC than the SA cofactors. The exception to this was the SSS-39 cofactor which produced very poor flocculation. For those cofactors containing sulfonated groups the best flocculation occurred when POLYPAM-CO-PEG was added to the system before the cofactor.

The sodium acrylate containing cofactors, however, produced better flocculation when they were added before the flocculant.

The solution concentration of $Ca^{2+}$ was found to play an important role in the flocculation ability of the acrylate cofactors. An increase in the $Ca^{2+}$ solution concentration (by the addition of $CaCl_2$ to the system from the equilibrium $Ca^{2+}$ concentration of 1.8 mM to 2 - 75 mM) led to a progressive decrease in the extent of flocculation induced by these SA cofactors.

An increase in calcium concentration had less of an effect on the sulfonated cofactors, with the exception of SSS-39 where a marked increase in flocculation resulted.

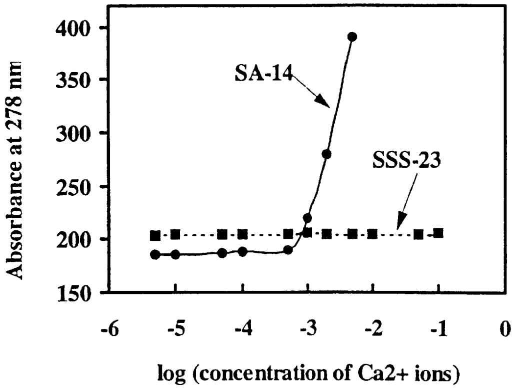
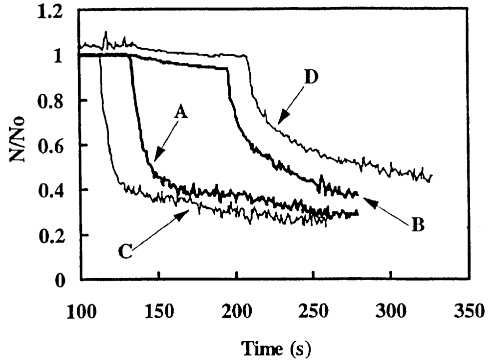


Figure 7 Turbidity data obtained from 2 cofactors which were dosed with increasing concentrations of $CaCl_2$. A calcium ion concentration of 0.6 mM induced precipitation of the SA-14 cofactor but the sulfonated cofactor, SSS-23, remained unaffected by a$CaCl_2$ concentration up to 100 mM.

The effect of calcium concentration on the cofactor solubility was investigated by measuring the turbidity of a cofactor solution as a function of the concentrations of $CaCl_2$. The results, summarized in Figure 7, show that increasing the $Ca^{2+}$ concentration from 0.5 to 1 mM caused an increased in turbidity indicating precipitation of the SA-14 cofactor.

Thus, we concluded that the relatively poor performance of the SA cofactors occurred because calcium ions induced precipitation of the cofactor preventing complex formation with the flocculants. Attempts to minimize this by decreasing the concentration of $Ca^{2+}$ (by the addition of $Na_2CO_3$ from 1.8 mM to 1.5-0.5 mM), had little or no effect of the ability on the cofactors to flocculate PCC.



| Run | Start | After PCC addition | Speed after addition of cofactor | Speed after addition of POLYPAM-CO-PEG | $N\backslash No_{(10s)}$ |
|---|---|---|---|---|---|
| A | 200 | 200 | 200 | 200 | 0.408 |
| B | 600 | 600 | 600 | 600 | 0.613 |
| C | 200 | 200 | 200 | 600 | 0.384 |
| D | 600 | 600 | 600 | 200 | 0.748 |

Figure 8 The effect of changing the propeller speed on the amount of flocculation induced. PCC (1,000 ppm), SSS-23 (2 ppm), POLYPAM-CO-PEG (2 ppm), pH 7.5, NaCl = $10^{-3}$ M, cofactor addition before flocculant addition. Note: the time axis is arbitrary, the steep descending part of each curve corresponds to the time of flocculant addition.

By contrast, calcium chloride concentrations as high as 100 mM did not induce precipitation of the SSS-23 cofactor. The relative insensitivity of sulfonic acid groups to calcium ions is well known in surfactant technology.

The flocculation results were dependent upon the stirring speed. The results summarized in Figure 8 show that flocculation, as judged by turbidity, decreased when the stirring speed was increased from 200 RPM to 600 RPM (compare runs A and B). Comparisons between runs A, C and D reveal that the cofactor addition step was the most sensitive to the stirring rate.

### b) PEO

The PCC flocculation results with PEO are also summarized in Figure 6. In contrast to the behavior of POLYPAM-CO-PEG, summarized in the last section, the SA cofactors were, in general, more effective than the SSS cofactors with PEO. As observed with POLYPAM-CO-PEG, neither the cofactor nor PEO alone induced flocculation.

An increase in the solution $Ca^{2+}$ concentration from 1.8 mM to 75 mM led to significant improvements in flocculation when the SSS cofactors were employed, but the performance of the SA cofactors was markedly reduced. A lowering of the $Ca^{2+}$ concentration resulted in the SA cofactors performing better than the SSS ones. Once again, this indicates that the SA cofactors were being precipitated out of solution by calcium ions.

### c) CPAM

Results obtained using cationic CPAM showed that the sulfonated cofactors induced markedly better flocculation of PCC than the sodium acrylate compounds. The higher the sulfonate content: the better the flocculation, SSS-39 inducing the maximum PCC flocculation using CPAM.

Altering the $Ca^{2+}$ concentration (either raising from 1.8 mM to 75 mM, or lowering from 1.8 mM to 0.5 mM) had a profoundly negative effect on the amount of flocculation induced; the flocculating ability of the SSS cofactors was markedly reduced whilst the SA cofactors were almost totally inhibited.

In general the PCC flocculation results summarized in Figure 6 are complicated. No single cofactor was best for every flocculant.

In the case of POLYPAM-CO-PEG, best flocculation was obtained when this flocculant was combined with SSS-23. When choosing a cofactor to combine with PEO, SSS-19 was the most effective whilst the cofactor which produced the best flocculation when combined with CPAM was SSS-39.

## $TiO_2$ FLOCCULATION

Colloidal $TiO_2$, with an average diameter of 210 nm, was dispersed in 0.001 M NaCl at pH 7.5. Under these conditions the oxide particles have negative surface charge. Flocculation experiments were conducted with a $TiO_2$ concentration of 186 ppm which gave a linear response in the PDA.

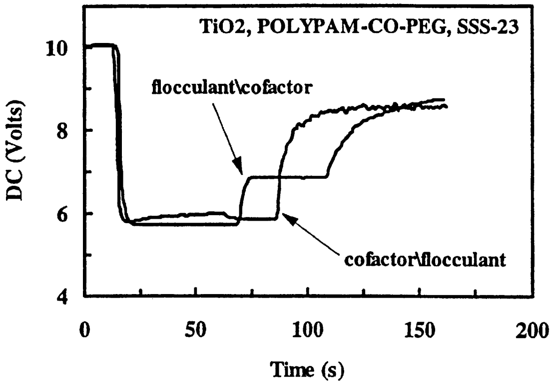


Figure 9 The influence of order of addition of cofactor and flocculant on $TiO_2$ flocculation using POLYPAM-CO-PEG and SSS-23. The addition of POLYPAM-CO-PEG alone caused flocculation, subsequent addition of cofactor causing further flocculation. When cofactor is the first component added no flocculation occurs until addition of POLYPAM-CO-PEG. The same total flocculation was obtained in each case.

### a) POLYPAM-CO-PEG

Unlike PCC, the addition of POLYPAM-CO-PEG alone to $TiO_2$ caused significant flocculation. This behavior is illustrated in Figure 9 which shows the PDA traces for two experiments; one in which POLYPAM-CO-PEG was added first and one in which the SSS-23 cofactor was the first component added.

When the cofactor was added first there was no indication of flocculation until both polymers were present. By contrast, when the flocculant was added there was an immediate decrease in turbidity. Subsequent addition of cofactor gave further flocculation. An explanation for this is that flocculant adsorbed on $TiO_2$ causing some bridging flocculation, with cofactor addition causing the flocculant coated particles to aggregate as shown below (Figure 10).

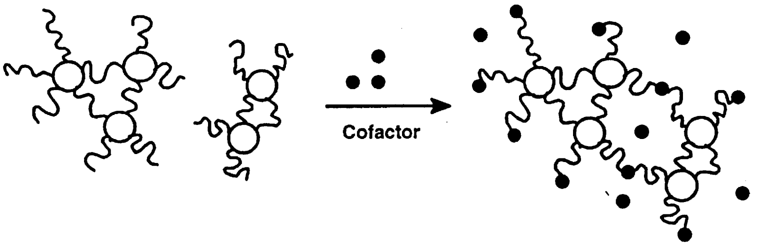


Figure 10 A postulated mechanism for the action of cofactors.

The flocculation behavior was sensitive to the ratio of POLYPAM-CO-PEG/cofactor. The results in Figure 11 illustrate this behavior.

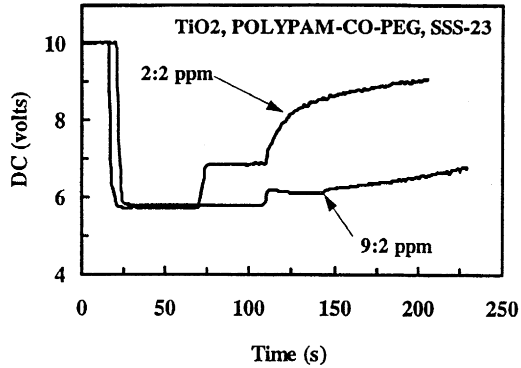


Figure 11 PDA traces showing the flocculation of $TiO_2$ induced by POLYPAM-CO-PEG followed by SSS-23. The labels give the concentrations of flocculant followed by cofactor.

When the mass ratio of flocculant to cofactor was greater than 2:2 (raising the surface coverage of polymer on PCC from 0.19 $mgm^{-2}$ to 0.85 $mgm^{-2}$) the flocculation was reduced; similar results have been reported for latex with this polymer system(28). The decreased extent of flocculation at high flocculant concentration, before cofactor addition, indicates that simple bridging was inhibited by too high a concentration of flocculant. This is classical behavior.

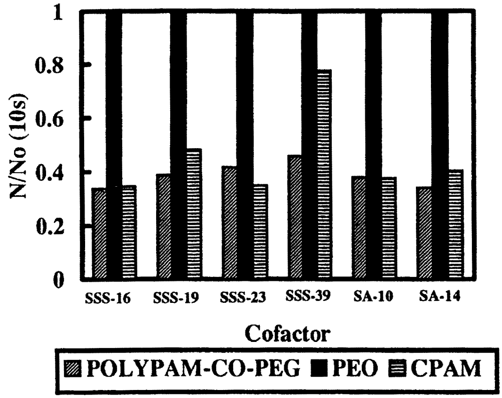


Figure 12 Flocculation results obtained for $TiO_2$. The cofactor (2 ppm) was added before flocculant (2 ppm) addition.

The $TiO_2$ flocculation results are summarized in Figure 12. The ability of the SA cofactors to flocculate $TiO_2$ was equal to that of the SSS cofactors. In this case there were no calcium ions present to precipitate the SA cofactors.

## b) PEO

Absolutely no flocculation of $TiO_2$ could be induced using any of the cofactors when PEO was the flocculant employed (see Figure 12). Dynamic light scattering was used to probe the adsorbed layer thickness of CPAM, PEO and POLYPAM-CO-PEG on $TiO_2$.

The results, summarized in Figure 13, show that the adsorbed layer thickness of PEO on $TiO_2$ is about 5 nm which is approximately equal to half the Debye screening length in 0.001M sodium chloride.

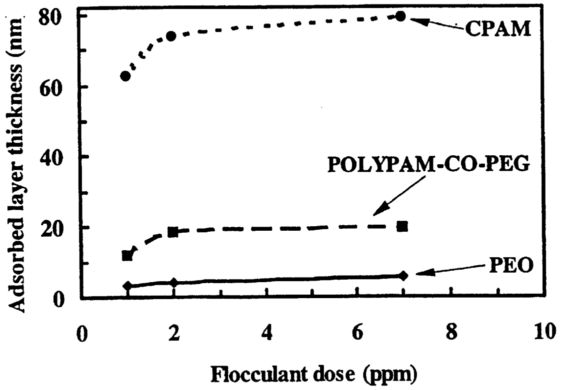


Figure 13 The apparent adsorbed layer thickness on $TiO_2$ particles (210 nm diameter).

Thus, it is proposed that electrostatic repulsion prevents the interaction of the anionic cofactors with PEO adsorbed on the $TiO_2$ surface. The apparent adsorbed layer thickness values for the other two flocculants was at least two Debye screening lengths.

When 0.5 mM of $MCl_2$ (where M = $Ca^{2+}$ or $Co^{2+}$) was added to the PEO system reasonable flocculation of $TiO_2$ was obtained. This was most probably a result of compression of the Debye screening length which made adsorbed PEO available for bridging.

### c) CPAM

CPAM induced flocculation of $TiO_2$ without the aid of a cofactor. This is to be expected because of the cationic nature of this polymer and the negative surface charge of $TiO_2$.

This result was similar to that obtained using POLYPAM-CO-PEG but, unlike the latter system, further flocculation was not induced when cofactor was added subsequent to CPAM.

In general the SA cofactors were equivalent to some of the SSS cofactors at inducing $TiO_2$ flocculation. An interesting point was that the SSS-39 cofactor showed a dramatic improvement in the amount of flocculation induced when the solution $Ca^{2+}$ concentration was increased from 0 to 0.5 mM using CPAM.

As with PCC, no single cofactor was best for every flocculant in the flocculation of $TiO_2$. PEO induced no flocculation of $TiO_2$ unless the Debye screening length was reduced by the addition of ions. When POLYPAM-CO-PEG was the chosen flocculant either SSS-19 or SA-14 induced the most flocculation. The cofactor SSS-23 proved to be the best when CPAM was employed.

## CLAY FLOCCULATION

Calcined kaolin, with an average particle size of $<2$ $\mu$m was dispersed in 0.001 M NaCl and the pH was adjusted to 7.5. Under these conditions the large faces of the clay plates have a negative charge whereas the edges are positively charged. The clay flocculation results are summarized in Figure 14.

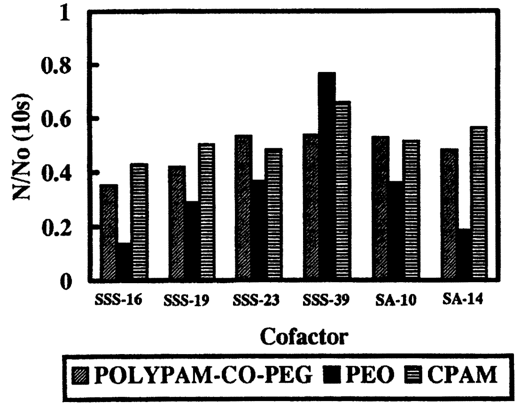


Figure 14 Flocculation results obtained for clay. The cofactor (2 ppm) was added before the flocculant (2 ppm) addition.

### a) POLYPAM-CO-PEG

The POLYPAM-CO-PEG flocculant caused significant flocculation of clay on its own but the subsequent addition of cofactor did not cause further flocculation. The best cofactors were those which contained small concentrations of sulfonic acid groups. However, as the sulfonate content increased the effectiveness of these cofactors to flocculate clay steadily decreased.

The acrylate cofactors did not improve on the flocculation of the sulfonated cofactors. The flocculation ability of all cofactors decreased when the $Ca^{2+}$ concentration of the system was increased from 1.8mM to 2-50 mM.

### b) PEO

PEO proved to be an extremely efficient flocculant of clay even without a cofactor. Subsequent addition of cofactor induced further flocculation. The cofactors which induced maximum flocculation were SSS-16 and SA-14.

The addition of $Ca^{2+}$ to the system (50 mM) caused a marked reduction in the amount of flocculation induced in all cofactors except SSS-39 where an increase in flocculation was observed.

### c) CPAM

The addition of CPAM on its own to clay resulted in flocculation. This was to be expected as the clay particles carry a negative surface charge, however, no further flocculation occurred when the cofactor was added. The most efficient cofactors were those containing low SSS content (SSS-16 and SSS-19). The acrylate cofactors induced reasonable flocculation whilst SSS-39 was the worst.

The addition of $Ca^{2+}$ to the system (up to 50 mM) resulted in no significant change in the amount of flocculation induced using any cofactor except SSS-39, where an increase was observed.

The flocculation of clay appears to be less complicated than that of either PCC or $TiO_2$. For each of the flocculants used, the best flocculation of clay was obtained when SSS-16 was used.

## 4. OTHER RESULTS

Some commercial cofactors form precipitates when mixed with PEO whereas others do not. The three flocculants were mixed individually with SSS-23 or SA-14 in 1500:1500 ppm. In no instance was a precipitate formed. Both PEO and CPAM flocculants, produced a gel with all cofactors. By contrast, POLYPAM-CO-PEG did not form a visible gel.

Cofactor SSS-23 was evaluated as a cofactor before hydrolysis using POLYPAM-CO-PEG and PCC. In this situation the phenolic groups were present as esters of acetic acid (see Figure 3). No flocculation was observed. This observation is further support for the proposal that the phenolic OH group is an important component of the cofactor.

## 5. DISCUSSION

The results obtained in this work show a wide range in the amount of flocculation induced, which was dependent on the components present in each system. However, the large data base of experimental results can be distilled to a few key findings. The first is that sulfonic acid containing cofactors are more calcium ion tolerant than are cofactors containing carboxyl groups. This effect is important in furnishes that contain calcium carbonate and may be important for deinked pulps which can have high calcium ion carryover from the deink plant.

Another striking feature of the results is that over the range of cofactor structures studied there was no clear best candidate. Different cofactors were better with the various combinations of colloids and flocculants. This may not be a general observation since this work sampled only a small range of possible cofactor structures. Other charge contents, branching and molecular weights will be evaluated in continuing work.

The polyvinyl phenol copolymers formed gels when mixed with PEO or CPAM indicating polymer/polymer complex formation. In addition to hydrogen bonding, the anionic cofactors would complex with cationic CPAM by electrostatic interactions. Also, we believe that hydrophobic interactions, first proposed by Stack and coworkers(18), are a crucial part of the cofactor/PEO system. Hydrophobic parts of the cofactor molecule could associate with PEO; it is well established that the hydrophobic surfactant tails associate with PEO by hydrophobic interactions(30).

The hydrophobic regions on the cofactor molecules should also facilitate adsorption of the cofactor and or the PEO/cofactor complex onto surfaces which, in turn, facilitates flocculation. We propose that the absence of hydrophobic interactions explains the inactivity of poly(acrylic acid) and poly(methacrylic acid) as cofactor flocculants. These acids are simply too hydrophilic to adsorb after complex formation.

Phenolic groups provide hydrogen bonding donor sites with pKa values low enough to give strong interactions and yet high enough not to dissociate under papermaking conditions. Also, the hydrophobic character of the aromatic rings contributes to the hydrophobic interactions.

We can speculate about the properties of the ideal cofactor. Clearly, sulfonic acid groups are the preferred solubilizing functionality because of calcium tolerance. Phosphonic acid groups may offer similar advantages however phosphonic containing cofactors have not been reported. The cofactor should have hydrophobic domains to give the interactions described above. However, if the cofactor is too hydrophobic, complexes with PEO will coacervate to form a precipitate which is not an effective flocculant.

The better current commercial cofactors do not form precipitates when mixed with PEO in water whereas the earlier commercial systems did. The microstructure of the cofactor may have to be controlled to give optimum hydrophobic interactions. For example, hydrophobic blocks or domains should give stronger interactions than isolated hydrophobic groups. On the other hand, large hydrophobic blocks will cause the cofactor to form micelles in water which may or may not be desirable for flocculation. Current work in our laboratory is aimed at testing some of these speculative concepts.

## 6. CONCLUSIONS

The non-ionic POLYPAM-CO-PEG flocculant required a cofactor to induce flocculation of all the colloidal dispersions studied in this work. PEO flocculated clay and CPAM flocculated both clay and $TiO_2$ without the aid of a cofactor.

The sodium acrylate-containing cofactors were very susceptible to precipitation by $Ca^{2+}$ ions.

With the sulfonated cofactors the presence of $Ca^{2+}$ ions could be advantageous. We speculate that adsorption of these cofactors onto anionic surfaces was enhanced by the presence of $Ca^{2+}$.

Over the range of cofactor composition studied no general conclusions could be made about the effects of cofactor structure on flocculation.

The best flocculation of PCC was obtained using POLYPAM-CO-PEG with a cofactor containing 23 mole % of sulfonated groups with a charge of 1.66 meq/g.

The best flocculation of $TiO_2$ was obtained using POLYPAM-CO-PEG with either SSS-19 a poly(vinyl phenol) cofactor containing 19 mole % of sulfonic acid groups, or with SA-14 a cofactor containing 14 mole % acrylic acid groups.

The easiest colloid to flocculate was clay. The best flocculation of clay was obtained using PEO with a SSS-19 cofactor.

## 7. ACKNOWLEDGEMENTS

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# Transcription of Discussion

## New information on the role of cofactors in PEO-type retention aid systems

*Professor Robert Pelton, McMaster University, Canada*

*Dr Richard Bown, Research & Technology Director, ECC, UK*

In order to clarify before we start, the clay used was a calcined clay not a hydrous clay and which has a fairly hydrophobic surface. I don't know if that influences your thinking in any way.

*Robert Pelton*

We have just started to work on this. We haven't developed a theory for this yet.

*Professor Per Stenius, Helsinki University of Technology, Finland*

You state that there is systematic knowledge about the nature of the complexes that are formed by the cofactors and PEO. It seems probable that the polymers form gels by associative phase separation. Did you try to map the phase equilibria in these systems? In your experiments you always used equal amounts of the two polymers. Did you try to vary the polymer ratio in order to verify whether the gel dissolves in the presence of an excess of either polymer? What is the minimum amount of the co-factors required to precipitate polyethylene oxide?

*Robert Pelton*

There are two fundamental different behaviours in co-factor systems. Some types of co-factors, the ones with lots of charged groups, are able to form complexes which do not precipitate. The complex looks like a gel. The other type of co-factor, perhaps with less charges and more hydrophobic areas forms complexes which undergo coacervation giving a black lump lying at the bottom of the beaker. I would be reluctant to talk about phase diagrams because I'm not sure you could ever get equilibrium structures with these systems. What we have done, following on from van de Ven, who worked with commercial co-factors, was trying to look at dynamic light scattering of dilute solutions. In that case you have to go off the optimum ratio of co-factor to PEO to get small enough things to study under dynamic light scattering. We have done some of this and the results will be reported.

*Theo van de Ven*

I have a comment about your cartoon which is a result for your experiment where you first add PEO and you reach one plateau and then you add the co-factor and then you have a second plateau.

*Robert Pelton*

That was an experimental result.

*Theo van de Van*

But after that you had a cartoon explaining it. Perhaps I could give a slightly different way of explaining it. We have seen that many co-factors increase the bond strength - if you have a plateau you obviously have a dynamic equilibrium between formation and break up of flocs and if you make the bond strengths stronger you shift the equilibrium towards larger and stronger flocs.

*Robert Pelton*

From what I've seen about floc reformation in our tensile tests. I'm really sceptical about reflocculation in any of these systems. I know we saw fibre flocculation data this morning but I think we really need a serious look at reflocculation. Having said that I think your explanation is possible, and a good one, so in terms of your jargon the escape probability goes down with stronger bonds.

*Juha Mentu, Microbiologist/Laboratory Manager, Enso Group Oy, Finland*

I think I understand what you are talking about. When such delicate compounds with very exact structures like these co-factors are to be applied in the rather contaminated water in the processes of the paper industry, it seems rather important to study also the biodeteriorative activity of process flora (microbes) on these chemical structures because these compounds may be broken down enzymatically if they are stored for long periods. Have you studied the resistance of these co-factors against such enzymatic breakdown?

*Robert Pelton*

No we haven't. I think that's an important step along the road of commercialising any new wet end chemical. We would expect an industrial partner to do that.
We also worry about producing things that are too toxic.