Interfacial Effects of a Polyalkylene Oxide/Fatty Acid Surfactant Blend in Flotation Deinking of Mixed Office Papers


ABSTRACT

The interfacial activity of a polyalkylene oxide/fatty acid surfactant blend in deinking flotation systems was examined through flotation, atomic force microscopy, zeta potential, contact angle, and surface tension studies. Based on laboratory flotation experiments using a Denver-type flotation cell, it was found that a gain of 10-14 points in brightness can be attained in one-stage deinking flotation of mixed office paper. Studies indicate that one of the major effects of the polyalkylene oxide/fatty acid surfactant blend is associated with its adsorption at the water-air interface and production of a stable froth. Secondly, examination of interfacial forces between a polyethylene particle (model “air bubble”) and a toner substrate showed significant enlargements of attractive hydrophobic forces in the presence of both polyalkylene oxide/fatty acid surfactant blend solutions and calcium ions. Although an energetic barrier was recorded between the polyethylene particle and toner substrate in the fundamental AFM studies involving solutions of low-ionic strength, this energetic barrier is practically non-existent in tap water. This suggests that the repulsive forces between gas bubbles and ink particles should be dominated by hydrophobic forces in daily mill operations, where process water with increased amount of dissolved ions is always used.

KEYWORDS

Atomic force microscopy, Contact angle, Deinking, Flotation, Interfacial forces, Office waste, Surface chemistry, Wastepaper.

INTRODUCTION

In today’s society, consumer product recycling has become a major issue, and paper recycling is no exception. Conservation of wood products, toxic emissions from traditional paper making methods, and new process technologies have made paper recycling a viable industry. However, a gap exists in efficiency between traditional and recycled paper making methods, mainly because of the added steps such as deinking flotation, washing, cleaning, bleaching, and screening of “stickies”. Therefore, the integration of the recycled paper products is largely determined by the extent of the ink removal and the ability to compete cost-effectively with traditional papermaking methods.

The technology found at modern paper recycling mills is on the cutting edge in terms of process technology, automation, and product quality. The separation process includes operations of repulping, washing, bleaching, flotation, and drying, resulting in approximately 90% of the ink/toner separated from the pulp. Sophisticated flow sheets have been developed in conjunction with air-sparged flotation cells to maximize ink particle removal. Flotation is often carried out in two stages, and as with any sort of industrial equipment, there are multitudes of parameters and operating conditions that can be varied to maximize performance including flow rate, temperature, pH, and reagent types among others. Flotation reagents used in paper recycling are generally termed “surfactants” or “surfactant blends” and can be broken down into two
main components: frothers and collectors. Modifiers of pH are usually added separately in the bleaching operation. Activators, such as calcium ions, come directly from the paper pulp, by dissolution of mineral filler (calcite), and are not added separately.

Surface effects in deinking flotation are a widely studied topic, in which the current knowledge has recently been reviewed in two monographs edited by Doshi and Dyer (1,2).

The objective of this study was to establish an understanding of the surface chemistry in deinking flotation for recovered mixed office paper in solutions of a Lionsurf® (polyalkylene oxide/fatty acid) surfactant blend. This was accomplished by carrying out experiments consisting of: flotation testing, atomic force microscopy, zeta potential measurements, contact angle measurements, and surface tension measurements. Lionsurf® surfactant blend was used in the experiments because it is an efficient component in the flotation deinking of mixed office paper at neutral and alkaline solution conditions in plant practice.

EXPERIMENTAL

Materials and Reagents

Experiments were carried out using resources donated from Great Lakes Pulp & Fiber paper recycling mill, whose feed consists of mixed office paper. Mixed office paper is principally composed of colored, photocopied, and laser printed paper. Pulp used in the flotation experiments was allocated from pulped, screened, and detrashed mixed office waste. Also, Lionsurf® surfactant blend (a mixture of polyalkylene oxide surfactant with fatty acid) was received from the operating plant.

Xerox Dry Ink Plus 5052/1050 was used as model ink particles in various experiments. It is composed of styrene/acrylate polymer (85-90%), carbon black (10-15%), amorphous silica (<1%), and zinc stearate (<1%).

Tap water was used in most of the experiments. The analysis report for this tap water provided by the Houghton City water department indicated the following quality: hardness 128 mg CaCO₃/L, chloride 28mg/L, sulfate 12 mg/L, and sodium 11 mg/L. Deionized water was also used in selected experiments.

Analytical grade calcium chloride and potassium hydroxide were purchased from Fisher Scientific.

Flotation Experiments

Testing was performed with Denver type, model D-1 flotation machines, which are used extensively in mineral flotation. The cell has a two-liter capacity, is mechanically agitated, and air is introduced at the bottom of the cell through the impeller. The air flow rate in the experiments was about 2.4 L/min. All tests were performed at a rotational speed of 1,400 rpm. By convention, 1% wt pulp was prepared using the paper pulp received from Great Lakes Pulp and Fiber mill and local tap water of varying temperature.

For the purpose of attaining reproducibility in the flotation experiments, a number of variables were specified, and kept constant for each test. The paper was pulped in approximately 200 ml of water and mechanically agitated for four min. In addition, the surfactant blend was conditioned for two min prior to flotation, and the residence time of the pulp was selected as five min, though it was observed that only 2-3 min was required. Concentration of surfactant in the pulp was maintained at 0.014 g/L, 0.028 g/L, and 0.042 g/L.

The flotation products were analyzed with a Technidyne TB-1C Brightness Meter at the Great Lakes Pulp and Fiber laboratory. The percent brightness was used primarily to determine the quality of the flotation products in this report. Note that in order to attain representative results it was necessary to prepare the pulp in such a manner that the surface was as smooth as possible.

In the flotation experiments where temperature was a targeted variable, the actual temperature of the system was represented by determining the temperature of the suspension prior to, and after flotation. An average of these values sufficiently represents the temperature of the system during flotation.

Atomic Force Microscopy

The interfacial force measurements between a model air bubble and toner substrate were performed using a Nanoscope E atomic force microscope (AFM) from Digital Instruments Inc. Details of this technique are discussed in a previous paper (3). All measurements were performed in a fluid cell using freshly prepared solutions with a rectangular tipless cantilever with a spring constant
of 29.7 N/m, also offered by Digital Instruments. Note that the measured force values have been normalized with respect to the radius of the model air bubble, the diameter of which was measured from scanning electron micrographs.

A polyethylene particle was used in the experiments as a substitute for air bubbles and was required in order to avoid the elasticity of the air-water interface. The precise measurements and subsequent interpretation of expected data for the systems with elastic interfaces is extremely difficult and can not be done with our current laboratory resources at this time. Although this is a simplification of the flotation system, previous results (3) show that such an experimental approach still leads to useful conclusions regarding the selection and nature of solution chemistry for deinking flotation. Polyethylene was selected because of its relatively uniform, homogeneous, and hydrophobic nature. The hydrophobicity of polyethylene is slightly less than for air; the interfacial tension between polyethylene and water is about 50 mN/m whereas this value is about 72 mN/m for an air/water interface at room temperature.

All experiments were performed with a 19 µm polyethylene particle, which was glued to the AFM cantilever by means of a micromanipulator and a CCD camera/monitor system. This procedure was carried out two to three days prior to AFM measurements to ensure the glue had properly set. Polyethylene particles used in the experiments were prepared according to the fabrication method described in Ref. (4).

A toner substrate with a smooth surface was prepared by melting the Xerox Dry Ink Plus 5052/1050 on aluminum foil at approximately 130 °C for about 30 min. The resulting toner substrate had micro-roughness features with a height ranging from 20 to 100 nm.

**Contact Angle Measurements**

A toner substrate was prepared by wrapping a petri dish with aluminum foil, on which the ink powder was placed at a thickness of approximately 1 mm. The sample was then put into a furnace at 130 °C for two hr. The ink particles were melted and formed a flat, glossy layer of ink. Advancing contact angles were then measured on such a prepared ink substrate with the sessile-drop technique (5). During advancing contact angle measurements the needle remained above the drop, and by adding more liquid the size of the drop was enlarged.

Measurements were performed on drops (of advancing volume) ranging in volume from 10 µl to 50 µl. Note that the contact angle was measured within 5-15 sec after the drop volume was increased, and that all measurements were done at room temperature (20 °C).

**Other Measurements**

Zeta potential measurements for toner particles suspended in water and aqueous solutions of polyalkylene oxide/fatty acid surfactant blend were done using Lazer Zee Meter Model 501 (Pen Kem, Inc.). A constant ionic strength was maintained in each suspension by dissolving 0.001 moles per liter of potassium chloride. To significantly improve the dispersion of particles in solution, suspensions of toner particles were prepared one week prior to zeta potential measurements by adding 0.2-0.4 g of toner to 200 mL of appropriate solution. The zeta potential measurements were done in less than 3-5 min after injection of the suspension into the electrophoretic cell.

The surface tension of water and surfactant solutions was measured by the pendant drop technique using a Kruss DSA System. These measurements were also done at a room temperature (20 °C).

**RESULTS AND DISCUSSION**

In this research program effects of a surfactant blend on the interfacial chemistry of flotation deinking were evaluated. On a practical level, several flotation experiments were carried out in order to test the performance of the surfactant blend in various conditions, such as at different surfactant concentrations and at different pulp temperatures. This was followed up with a more fundamental examination of the surface effects in flotation deinking. The main properties of interest were the zeta potential and the hydrophobicity of toner particles, the surface tension of aqueous surfactant solutions, and the interfacial forces acting between a toner substrate and a "model" air bubble. Based on the experimental results obtained, the role of the polyalkylene oxide/fatty acid surfactant blend in flotation deinking is briefly discussed in this paper. It should be noted that technical difficulties associated with measurements of interfacial properties at elevated temperatures limited these experiments to room temperature.
Deinking Flotation Tests

Flotation in the presence of polyalkylene oxide/fatty acid surfactant blends at room temperature increased the brightness of the fiber product to 63-64% from samples received from Great Lakes Pulp and Fiber assaying at 54% brightness (Fig. 1). The surfactant concentration in the flotation tests was 0.028g/L, though it was found that the flotation results at surfactant blend concentrations ranging from 0.014 g/L to 0.042 g/L did not have any strong impact on the quality of the pulp product. However, a detailed study of flotation kinetics was not targeted, and the possibility that increased surfactant blend concentrations had an effect on the kinetics of ink removal from the pulp cannot be eliminated. Experiments beyond 0.014-0.042 g/L concentrations were not conducted, as the flotation tests were confined to common mill practice.

The efficiency of deinking flotation was also tested on office paper pulp received from the paper mill using several other Vining Industries surfactant blends (not shown). It was observed that these other surfactant blends had either similar or lower ink collecting abilities (brightness of the fiber product varied from 63 to 65%).

The effect of temperature on flotation deinking was of special interest due to the fact that most paper recycling mills carry out flotation processes at elevated temperatures, usually in the range of 40 to 60 °C. The effect of flotation temperature on the brightness of fiber product is shown in Fig. 1. Figure 1 clearly shows that increasing the operating temperatures from about 25 to 75 °C improves the quality of the fiber product. For example, fiber brightness of up to 68-69% was reached at 70-75 °C operating temperature in single stage, flotation tests.

The pH of the pulp and surfactant solutions used in all reported flotation experiments was at a pH of 7.0 ±0.2. Also several experiments were performed in solutions of pH 6.0 and 9.0 in this study, but the results did not indicate any increase in efficiency of deinking. It was already found in the previous studies with the surfactant blend that the flotation of ink from mixed office paper pulp is superior under neutral and slightly acidic pH conditions (6).

Zeta Potential of Toner

Flotation deinking is affected by the surface charge of particulates suspended in the pulp. Surface charges can either enhance or hinder bubble-particle (toner, mineral filler, and cellulose fiber) interactions and supply the driving force for the adsorption of surfactant. It is for this reason that a number of tests were conducted to determine the effect of polyalkylene oxide/fatty acid surfactant blend solutions on the zeta potential of toner particles.

Figure 2 shows the zeta potential of Xerox 5052/1050 toner versus pH in a 0.001M KCl solution. Experimental data shows that the toner carries a negative charge in water, which becomes less negative with a corresponding decrease in the pH of solution. The isoelectric point is located around pH 2.3.

It was found that polyalkylene oxide/fatty acid surfactant blend had a minor effect, if any, on the zeta potential of toner (Table 1), which is consistent with our expectation as a nonionic surfactant is the major component of the blend. The surfactant blend also consists of fatty acids, which adsorb on the toner surface. However, adsorption of a dissociated form of fatty acids is reduced by the repulsive electrostatic forces between the negative charge of the dissociated carboxylic group and the negative charge of the toner particles. It is expected that the addition of calcium ions to the surfactant solutions could improve the precipitation of calcium carboxylate species on the toner surface and affect, to a certain extent, the zeta potential values. Colloidal precipitates of Ca-carboxylate contaminated the toner particle suspension and introduced technical problems with zeta potential measurements that could not be overcome.
Hydrophobicity of Toner

Toner hydrophobicity is a crucial parameter in deinking flotation, the kinetics of which are dependent on the probability of attachment of the toner particles to gas bubbles. For the attachment of a toner particle to a gas bubble to occur, a minimum degree of hydrophobicity is required, i.e., the contact angle is greater than zero. Contact angles that are significantly higher than zero accelerate the flotation process.

The advancing contact angles for water and polyalkylene oxide/fatty acid surfactant blend solutions on the surface of melted toner varied from approximately 80 to 90 degrees (Fig. 3 and Table 2). The contact angle measurements were conducted using the sessile-drop method for varying volumes of the drop. Selected examples of the relationship between advancing contact angle and drop volume are shown in Fig. 3. No significant effect of drop volume on advancing contact angle was found in this study in the range of approximately 15 µL to 35-50 µL and thus, average values of contact angles were calculated. The results are shown in Table 2.

Advancing contact angles measured for the toner substrate clearly indicate a high hydrophobicity of photocopy toner. However, a slight decrease of advancing contact angles on the toner substrate was noted when measurements were done with polyalkylene oxide/fatty acid surfactant blend solutions. This decrease was only a few degrees and probably was primarily caused by a reduced surface tension of solution (Table 2). More importantly, it was found that the hydrophobicity of toner was restored or even improved when calcium ions were added to the polyalkylene oxide/fatty acid surfactant blend solutions (Table 2). This tendency was observed for other surfactant blends and sodium laureate solutions as well (not shown). In many cases, the advancing contact angles even increased 2-4 degrees beyond the values measured on the toner surface for pure water. This indicated that additional hydrophobic species could adsorb/precipitate on the surface of toner whenever calcium ions were added to the fatty acid solutions.

Interfacial Forces

Microscopic forces such as electrical double layer, van der Waals, and hydrophobic forces can be investigated with atomic force microscopy. This relatively new technology was used to determine the effect of polyalkylene oxide/fatty acid surfactant blend on interfacial forces involved in a model deinking flotation system (polyethylene particle-aqueous solution-toner).

The relationships between measured forces and polyethylene particle-toner substrate separation are shown in Fig. 4. Note that the forces are normalized per radius of the polyethylene particle used in the experiments. Experiments were carried out in deionized and tap water, and in tap water solutions of polyalkylene oxide/fatty acid surfactant blend - with and without calcium ions. It should be added here that force/radius versus distance curves

<table>
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<tr>
<th>Table 1. Zeta Potential Values for Toner Particles Suspended in Water and Polyalkylene Oxide/Fatty Acid Surfactant Blend Solutions at pH 7.0±0.3.</th>
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<tbody>
<tr>
<td>Water Used</td>
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<tr>
<td>----------------</td>
</tr>
<tr>
<td>1. deionized water + 0.001M KCl</td>
</tr>
<tr>
<td>2. tap water</td>
</tr>
<tr>
<td>3. tap water</td>
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<td>4. tap water</td>
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<td>5. tap water</td>
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similar to that shown in Fig. 4 were recorded for another surfactant blend, but are not included in this report.

It is shown in Fig. 4 that strong repulsive forces acted between the toner substrate and polyethylene particle in deionized water at distances less than 25-30 nm. These repulsive forces are due to the overlapping of electrical double layers of negatively charged toner (see section on zeta potential measurements) and polyethylene surfaces. However, the electrical double layer forces were difficult to discriminate in tap water (Fig. 4). The ions dissolved in tap water compressed electrical double layers at the surfaces of the toner substrate and polyethylene particle, and the energy barrier between toner and polyethylene was almost completely eliminated; this has important practical consequences. Because paper recycling mills use tap water consisting of a large amount of recirculation, there are a significant amount of ions dissolved in the process water to reduce the (repulsive) electrical double layer forces arising in a microscopic event of a bubble-particle attachment. Consequently, attractive hydrophobic forces (see next paragraph) probably dominate the flotation deinking system, involving hydrophobic ink/toner particles. In addition, strong attractive forces were observed between the toner and polyethylene particle in

<table>
<thead>
<tr>
<th>Solution</th>
<th>Surface Tension [mN/m]</th>
<th>Advancing Contact Angle [deg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. water (pH 7)</td>
<td>72.0</td>
<td>87±2</td>
</tr>
<tr>
<td>2. 0.042 g/L polyalkylene oxide/fatty acid (pH 7)</td>
<td>53.4</td>
<td>79±4</td>
</tr>
<tr>
<td>3. 0.042 g/L polyalkylene oxide/fatty acid 5x10^4 M CaCl₂ (pH 7)</td>
<td>65.3</td>
<td>88±3</td>
</tr>
<tr>
<td>4. 0.042 g/L polyalkylene oxide/fatty acid (pH 9)</td>
<td>55.7</td>
<td>83±3</td>
</tr>
<tr>
<td>5. 0.042 g/L polyalkylene oxide/fatty acid 5x10^4 M CaCl₂ (pH 9)</td>
<td>63.9</td>
<td>87±4</td>
</tr>
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Figure 3: The effect of drop volume on advancing contact angle for aqueous solutions on toner substrate measured with sessile-drop method. Solutions (pH 7) used: 1) water (triangles); 2) 0.042 g/L Lionsurf® (squares); 3) 0.042 g/L Lionsurf® + 5x10^4 M CaCl₂ (diamonds).
deionized and tap water at distances less than about 12 nm and 16 nm, respectively (Fig. 4A). It is understood that these forces have their origin in the hydrophobicity of toner and polyethylene surfaces (Table 2 and Ref. 7, 8). Though, a difference in the range of hydrophobic forces was observed in experiments involving either deionized or tap water (Fig. 4A). The source of this difference could not be identified in this study. However, in this particular case, the measurements were done with different polyethylene particles and toner substrates and thus, small defects and irregularities on the solid surface(s) could contribute to the variation of experimental data. A difference in the chemistry of deionized and tap water associated with dissolved ions and gases could also contribute to experimental variation.

It was also found that an addition of polyalkylene oxide/fatty acid surfactant blend to tap water had only a small effect on interactions between a toner substrate and polyethylene particle. This can be seen in Fig. 4B where the curves of force/radius versus distance (F/R vs. H) were similar for both

*Figure 4: Interfacial forces versus distance measured for polyethylene particle-aqueous phase-toner substrate system. The pH value of aqueous phase was maintained at pH 7.0±0.3.*
tap water and 0.042 g/L polyalkylene oxide/fatty acid surfactant blend solution. In addition, a small energetic barrier was observed in the F/R vs. H curve for polyalkylene oxide/fatty acid surfactant blend solutions as compared to tap water (Fig. 4B). This small energetic barrier in the F/R vs. H curve could indicate adsorption of fatty acids (with dissociated carboxylic groups exposed to the aqueous phase) on toner, polyethylene, or both surfaces. Hydrophobic forces practically remained the same magnitude and range in both tap water and polyalkylene oxide/fatty acid surfactant blend solution (Fig. 4B). This scenario changed when calcium ions at an amount of 0.0005 M were added to the polyalkylene oxide/fatty acid surfactant blend solution (Fig. 4B). Two observations are worth note after the addition of calcium ions: the energetic barrier in the F/R vs. H curves was eliminated, and the magnitude of hydrophobic (attractive) forces increased in the presence of calcium ions. The range of the hydrophobic forces sometimes increased as well (not shown). This improvement in hydrophobic forces has significant consequences in deinking flotation as it most likely increases the probability of bubble-toner particle attachment, and the kinetics of toner flotation.

The Role of Surfactant Blend in Flotation Deinking

Flotation reagents used in paper recycling are generally termed “surfactants” or “surfactant blends,” but usually can be broken down into two main components: frother and collector. Frothers are used to build a stable froth layer that allow the separated ink particles to be skimmed from the top of the flotation cell, and are used to influence the size of gas bubbles. In the case of this study, nonionic surfactant such as polyalkylene oxide serves mainly as the frother.

The collector’s main purpose is to promote the selective attraction of the ink particles and mineral fillers to air bubbles. Fatty acids have been successfully implemented in the paper recycling industry and are an ingredient of the surfactant blend used in this study. However, fatty acids are ineffective in improving the attractive forces between bubble-water and ink-water hydrophobic interfaces if they are dissolved in the pulp without an activator. It is a well-known fact in flotation deinking that calcium ions activate the action of fatty acids (3, 9-11). This appears to be quite obvious from the fundamental studies of contact angle measurements and atomic force microscopy. First, the attractive forces between a “model” air bubble and toner significantly increased when the surfactant blend, containing fatty acids, was assisted by calcium ions (Fig. 4 and discussion in the previous section). Second, contact angle results showed that the hydrophobicity of toner increased in the surfactant blend solutions with calcium ions (Fig. 3 and discussion on hydrophobicity of toner). In full-scale plant operations, the calcium ions are usually not intentionally added to the recovered paper pulp. Calcite, as filler, is a component of many papers and dissolves in the process water during recycled paper pulping and mixing, providing source of calcium ions. It was also found, through the X-ray diffraction analysis of paper ash, that calcite is the major inorganic filler of the mixed office paper tested in this project (not shown).

CONCLUSIONS

Laboratory experiments conducted in a 2L Denver-type flotation cell showed that a gain of about 10 points in brightness can be reached in one-stage flotation of mixed office waste using the Lionsurf surfactant blend solutions at neutral pH conditions and at room temperature. Increasing the temperature to 70-75 °C provides a further gain of 3-4 points in fiber brightness.

Fundamental surface chemistry research presented in this paper supports interfacial activity of the polyalkylene oxide/fatty acid surfactant blend in deinking flotation systems, and the following effects were observed:

- the surfactant blend reduced the surface tension of water and produced a stable froth;
- no significant effect of the polyalkylene oxide/fatty acid surfactant blend was observed on zeta potential of toner;
- a high hydrophobicity of toner was only slightly affected by the polyalkylene oxide/fatty acid surfactant blend at concentrations less than 0.042 g/L;
- the interfacial force measurements between the polyethylene particle (model “air bubble”) and toner substrate revealed existence of strong hydrophobic forces at distances of less than 12-20 nm. These attractive hydrophobic forces were enlarged in the presence of both polyalkylene oxide/fatty acid surfactant blend and calcium ions. Also, an energetic barrier was recorded between the polyethylene particle and toner substrate in
deionized water and solution of the polyalkylene oxide/fatty acid surfactant blend indicating that the electrical double layer repulsive forces are stronger than attractive hydrophobic forces in the aqueous phase of low ionic strength. In flotation deinking practice, such energetic barriers between gas bubble and ink particles might slow down the kinetics of flotation.

It was found in the AFM study that the inorganic ions that are present in tap water compressed the electrical double layers around polyethylene and toner to such a degree that hydrophobic forces dominated in the model “air”-aqueous phase-toner systems. This observation has important practical implications indicating that the process water used in the paper recycling mill should carry enough dissolved ions to eliminate the negative effect of an energetic barrier associated with negative surface potentials on water-air and ink-water interfaces, on the attachment of ink particles to gas bubbles.

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LITERATURE CITED


