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KEYWORDS: MILLED WOOD LIGNINS, HYDROGENATION, AROMATIC COMPOUNDS, INHIBITION, YELLOWING, CATALYSTS, OXYGENATION, RHODIUM COMPOUNDS, LIGNIN MODEL COMPOUNDS.

The Effect of pH on Pulping and Flotation of Mixed Office Wastepaper

M.A.D. AZEVEDO, J. DRELICH and J.D. MILLER

The effect of pulping reagents on the deinking flotation of laser-printed wastepaper was investigated with regard to the removal efficiency of toner and mineral filler particles at different pH values. These results show that caustic pulping causes the toner to be released from the fibres as larger particles and a poor flotation response is obtained. On the other hand, neutral pulping not only causes the toner to be released as smaller particles but also increases the simultaneous flotation removal of toner and mineral filler particles. On the basis of these flotation results and atomic force microscopy force experiments, it is known that the remarkable removal of mineral fillers and toner particles under acidic conditions is related to the heterocoagulation of toner and filler particles.

L'effet des réactifs de trituration sur la flottation des vieux papiers d'imprimante laser lors du désencrage a été étudié en rapport avec l'efficacité de l'extraction des particules de toner et de charges minérales à diverses valeurs de pH. Ces résultats indiquent que, lors de la trituration à la soude caustique, le toner se dégage des fibres en plus grosses particules, ce qui entraîne une mauvaise flottation. Par contre, la trituration neutre permet non seulement au toner de se dégager des fibres en plus petites particules, mais aussi d'enlever simultanément par flottation les particules de toner et de charges minérales. Sur la base de ces résultats en matière de flottation et des essais de force par AFM, nous savons que l'extraction remarquable des particules de toner et de charges minérales dans des conditions acides est reliée à l'hétérocoagulation des particules de charges et de toner.

INTRODUCTION

Contaminant removal, essential to convert wastepaper into reusable cellulose fibre, is a major objective of wastepaper recycling. The efficiency of this removal determines the yield and cost of the final product.

Generally, ink is considered to be the principal deleterious contaminant due to its darkness. Ink varies in composition [1] and is present in different forms (liquid or dry ink) depending on the printing process. The quality of the clean fibre product is determined by the extent of ink removal.

The second major contaminant especially for mixed office wastepaper (MOW) is the mineral filler material. Retention of fillers by the recycled fibre leads to reduced fibre–fibre interaction and consequently to a reduction in the fibre web strength [2]. The mineral filler content of paper varies with the paper grade. Typically, mineral filler will comprise at least 12% of the paper, and it often represents an even larger portion of the total paper weight, reaching as much as

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40% [3].

In order to remove the ink and mineral fillers it is necessary to release them from the cellulose fibres. Usually, the contaminants are released by the action of heat, agitation and reagents. Once the contaminants are released from the fibres they are separated from the wastepaper pulp by washing [4] and flotation [5–8]. Both methods are used in combination since washing is less effective in the removal of larger ink particles (>20 μm), while deinking flotation is less effective in the removal of small ink particles (<20 μm). However, small toner particles can be removed by flotation, particularly if particle–particle aggregation can be induced to form larger toner aggregates [9].

During washing and deinking flotation, mineral filler particles are also removed simultaneously with the ink. It should be mentioned that both deinking methods were designed with the specific objective to remove ink particles rather than mineral filler particles. Washing is considered an efficient method for the removal of mineral fillers because of the small size of the filler particles (<2 μm) and it is for this same reason that deinking flotation is considered to be less efficient for mineral filler removal. Also, it has been reported that the inefficiency of mineral filler flotation is related to the alkaline conditions of the pulp [2]. It is a usual practice in recycling mills to have a washing stage after alkaline flotation in order to remove residual mineral fillers from the furnish.

The objective of this work was to study the release of contaminants and deinking flotation response of MOW under different conditions, in order to improve the removal of toner and mineral filler particles from the pulp. In addition, forces between toner and mineral filler (anatase) have been measured by atomic force microscopy (AFM) to determine the possible interactions between these materials at different pH values.

METHODS AND MATERIALS

Material

The wastepaper used for all experiments was generated using Xerox 4200 DP 20 lb copy paper. This paper contains kaolinite and anatase (TiO_2) as the major mineral fillers. The Xerox 4200 copy paper was printed with a Hewlett Packard laser jet III printer. The toner used was the Canon EP-S toner composed mainly of styrene–acrylate copolymer, styrene polymer, iron oxide and minor constituents.

Pulping and Flotation

Two types of pulping conditions were investigated. One condition was with the addition of sodium hydroxide (0.5 wt% of dry paper) for alkaline pulping at pH 10.0. The other condition was without the addition of reagents for neutral pulping at pH 5.0. For easy reference to these pulping conditions, they will be designated as alkaline and neutral pulping.

The pulping consisted of disintegration of the wastepaper structure and dispersion of the fibres. The disintegration was accomplished by conditioning 250 g of wastepaper, cut into small pieces, with deionized water, hot steam (84–90°C), and reagents as desired under moderate agitation. After disintegration, the pulp was further dispersed in a high-speed blender. All pulping experiments were done at a consistency of approximately 12% solids by weight.

Pulping for all deinking flotation was carried out under identical conditions to produce the same degree of dispersion prior to flotation. It should be noted that this is not necessarily the optimum condition for ink removal. The pulped wastepaper was diluted in a 4 L flotation cell to a consistency of 1% and conditioned for 2 min in the presence of the collector LIONSURF 768 (2% by weight based on the weight of the dry paper) as provided by Lion Industries. LIONSURF 768 is polyalkylene oxide surfactant blend with fatty acid. The flotation was then carried out for 15 min at a stirring speed of 1400 rpm. Subsequently, the float (toner particles) and nonfloat (cellulose fibre) products were carefully filtered, dried and stored for analysis of dirt removal and analysis of mineral fillers.

The dirt removal was determined by an image-analysis system developed at the University of Utah [10] by following the standard TAPPI procedure [11]. Analysis of the mineral fillers was done by DCP (direct current plasma) analysis following the procedure described in the literature [12]. The kaolinite was determined by the amount of aluminum (Al) while the anatase by the amount of titanium (Ti).

Atomic Force Microscope

Force measurements were conducted using a Nanoscope E atomic force microscope (Digital Instruments, Inc., Santa Barbara, CA, USA). A single laser printer toner particle (18 μm) was mounted on the AFM cantilever tip using a speed bonder and an activator (Loctite Corporation, Mexico City, Mexico) by means of a micromanipulator and a CCD camera/monitor system. The toner particle glued onto the cantilever has a rough spherical shape and was selected directly from the Canon toner cartridge. All interaction forces, between toner particles and mineral filler substrates, were measured in an aqueous environment (10^{-3} mol/L KCl) as a function of pH. The normalization of the forces and preparation of the force versus separation distance curves were obtained from the raw data by using an AFM analysis program [13].

In this study, it was possible to measure only the toner interaction force at the surface of a single crystal of anatase (TiO_2). In the case of kaolinite it was not possible to build a stable substrate surface.

Force measurements were repeated several times for each experiment in order to assess the reproducibility of the experiment. The force measurement error was found to be within 5% of the reported value.

RESULTS AND DISCUSSION

Pulping

In Table I, the particle size distribution for released toner particles is presented for neutral and alkaline pulping. As can be noted, alkaline pulping generated, on average, larger toner particles (390 μm) than neutral pulping (188 μm). These results suggest that NaOH, which was used for the alkaline pulping, has a strong influence on the release of toner particles.

The effect of NaOH in the release of larger particles can be explained as follows. The caustic solution, trapped in the fibres, may lubricate the system and reduce the abrasion responsible for the generation and release of the fine toner particles. Also the caustic swelling of the fibre may promote release of the larger toner particles [14,15].

The use of caustic conditions for the release of toner from MOW appears to be unnecessary. The practice of caustic pulping originates from the success in the deinking of old newsprint (ONP). However, the ONP paper is printed with oil-based inks. Such inks are removed from the paper by a saponification reaction [2].

The optimum particle size for flotation deinking is from 10 to 100 μm [2]. As a result of the smaller particle size generated by neutral pulping, a more efficient flotation deinking may be expected as compared to alkaline pulping conditions.

Flotation

Figure 1 shows the deinking flotation response for alkaline pulping (pH 10.0), specifically the extent of toner and filler removal at different flotation pH values. As can be observed, the removal of toner, anatase and kaolinite, as a function of flotation pH, is similar and goes through a maximum between pH 5 and pH 7.0.

In the case of neutral pulping (pH 5.0; Fig. 2), the overall removal of toner and anatase particles improves considerably when compared to the results for alkaline pulping. Once again the maximum removal is achieved between pH 5.0 and pH 7.0.

The inefficient ink removal for the alkaline pulping case can be related not only to the large toner particle size but also to the toner's surface properties. Contact angle

TABLE I
SIZE DISTRIBUTION OF TONER PARTICLES AFTER PULPING

Pulping Conditions	Range of the Ink Particle Size (μm)	Average Ink Particle Size (μm)
Neutral (pH 5)	10–400	188
Alkaline (pH 10)	45–600	390

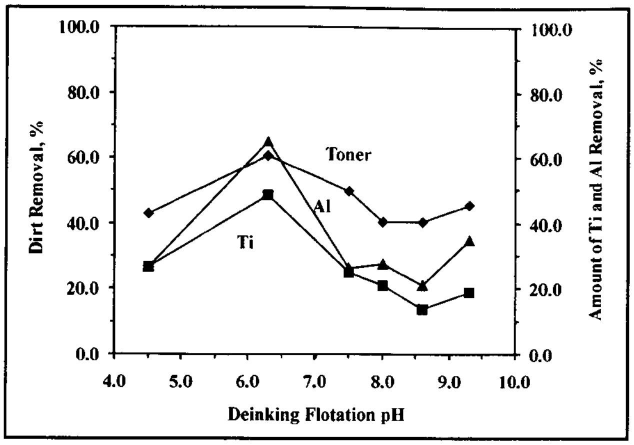

Fig. 1. Deinking flotation response with respect to the removal of toner particles and mineral fillers anatase (Ti) and kaolinite (Al) for laser-printed wastepaper pulped under alkaline conditions (pH 10.0).

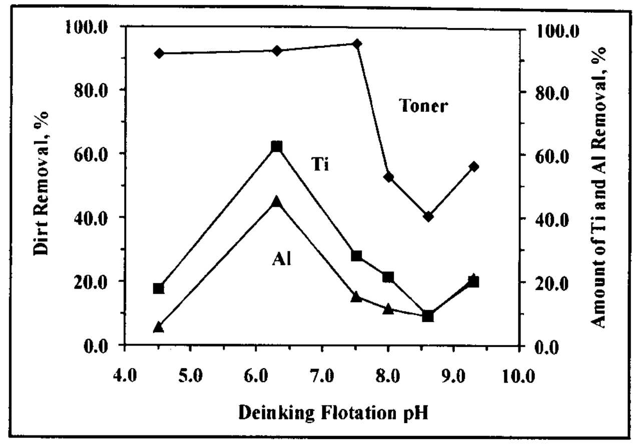

Fig. 2. Deinking flotation response with respect to the removal of toner particles and mineral fillers anatase (Ti) and kaolinite (Al) for laser-printed wastepaper pulped under neutral conditions (pH 5.0).

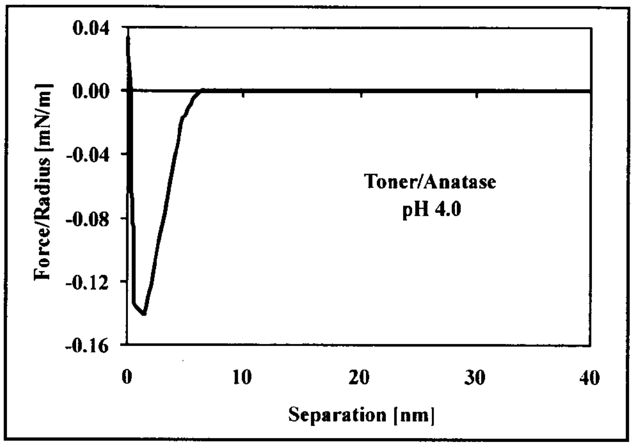

Fig. 3. Normalized force vs separation distance curve (approach curve) for toner and anatase system under acid conditions in presence of 10^{-3} mol/L KCl.

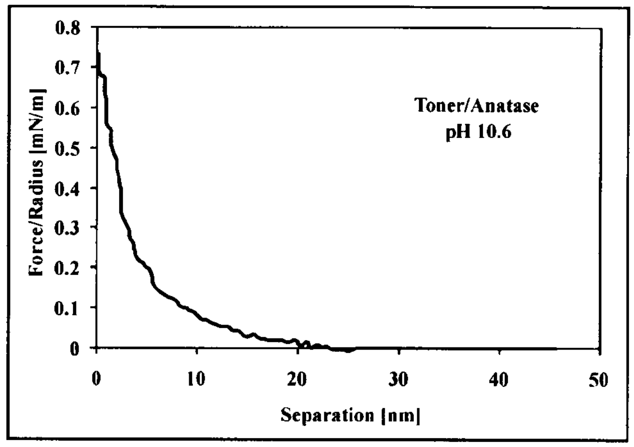

Fig. 4. Normalized force vs separation distance curve (approach curve) for toner and anatase system under alkaline conditions in presence of 10^{-3} mol/L KCl.

measurements have been reported for laser-printed toner films treated with caustic solution at elevated temperatures [16]. On the basis of these measurements, it is known that both elevated temperature and alkaline conditions significantly change the wettability of the toner particles. The alkalinity promotes a drastic decrease in the contact angle from 105–115° to 75–80°. Therefore, the caustic pulping environment not only promotes the release of larger particles but also reduces the hydrophobicity of the toner particles.

Independent of the pulping conditions, toner removal by flotation improves for pH values between 5.0 and 7.0. The reason for this improvement is uncertain. There is no change in the sign of the toner surface charge in this pH range (point of zero charge (PZC) around pH 2). Since the collector is a blend of polyakylene oxide with fatty acid, it is expected, under natural conditions, that the fatty acid species are no longer dissociated. The species are present in the acid form and may even precipitate as colloidal particles. It appears that the adsorption of the acid form may account for the increase in the hydrophobicity of the toner surface and consequently enhance its removal by flotation. However, such an explanation is speculative and does not account for the decrease in flotation below pH 4.5 for alkaline pulping.

Acidic conditions not only increase the removal of toner but also the removal of the mineral fillers. The explanation for such improvement can be partially related to the reversibility of the mineral filler surface charge with respect to pH. Anatase has a PZC that varies between pH values of 4.7 and 7.0 depending upon the mineral source and method of preparation. The same is true for kaolinite, in which case the PZC values vary from 4.0 to 5.0 depending upon the mineral source and method of preparation. Therefore under acid conditions both mineral fillers may have a surface charge opposite to that of the toner particles.

The coincidence observed for the shape of the flotation curves (Figs. 1, 2) suggests that the removal of mineral fillers may be related to the removal of toner particles. Perhaps the free mineral filler particles (less than 2 μm) interact with the larger (40–400 μm) and naturally hydrophobic toner particles and consequently they are removed together. This mechanism of heterocoagulation is similar to the carrier flotation phenomenon used to remove contaminants (anatase) from clay, in which case coarse calcite particles are introduced as carriers for heterocoagulation with fine anatase impurities from clay [17].

The carrier mechanism between calcite and anatase is based on hydrophobic attractive forces since both particles are covered with surfactant. In the toner/filler system, the hydrophobic force may not be the major force to account for the aggregation but instead electrostatic interaction may cause the heterocoagulation since both toner and filler are oppositely charged under acidic to neutral conditions. However, the surface charge of these particles in the presence of the collector has not been determined.

AFM Experiments

Figure 3 shows the interaction force obtained by AFM (approach curves) for the toner and anatase system at pH 4.0. As can be noted, an attractive force is observed between toner and anatase, indicating that these surfaces are oppositely charged and such a system would have a natural tendency to heterocoagulate. Attractive curves such as the one presented in Fig. 3 were observed for pH values between pH 4.0 and 7.0.

For alkaline pH values, repulsive forces were observed as shown in Fig. 4. These results were expected since both toner and anatase are negatively charged at pH values exceeding pH 7.0.

In order to verify the possibility of heterocoagulation of toner particles with mineral fillers, particle interaction experiments were conducted with cured toner and anatase in water at different pH values. It was found under acid conditions that anatase particles attach to the cured toner surface (see Fig. 5). At a pH value above 7.0, such attachment does not occur (cured toner is toner which had undergone a treatment similar to that encountered in the copying process). The same response was observed when the interaction of kaolinite particles with the toner surface was studied.

The success of toner and mineral filler flotation under neutral flotation conditions might also be related to the stability of the froth. It was observed experimentally that for neutral flotation conditions the froth stability increased considerably compared to the froth behaviour for alkaline flotation conditions.

According to the results presented, deinking flotation of laser-printed waste is more effective if it is operated under neutral pulping conditions because of the overall enhancement in the removal of toner and mineral filler particles. Another advantage of neutral pulping and flotation is that the chemical cost and the treatment cost of the water circuit is reduced due to low chemical oxygen demand and biological oxygen demand levels [2].

CONCLUSIONS

It appears that caustic pulping reduces the abrasive action and/or causes the fibre swelling, both of which result in the release of larger toner particles. In the absence of caustic solution, the toner particles are released at a smaller size.

Independent of the pulping conditions, the deinking flotation response is strongly affected by changes in flotation pH. It was shown that the removal of both toner and mineral filler is significantly improved under acidic to neutral pH conditions as compared to the results for conventional alkaline pH.

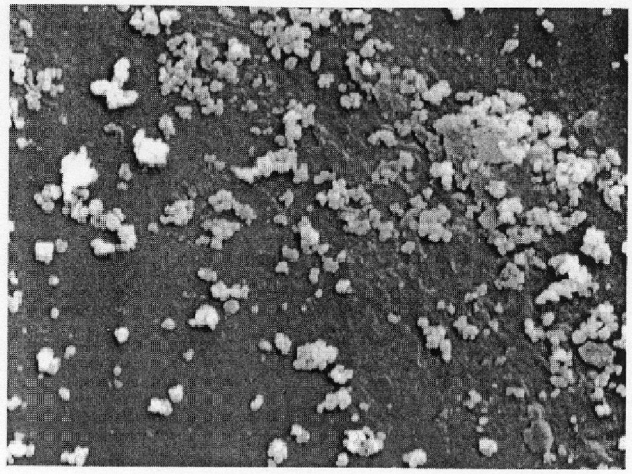

Fig. 5. Attachment of anatase particles on a cured toner surface at pH 4.8 (×6820).

Both force measurements and particle interaction experiments confirmed that the remarkable removal of mineral filler at acidic conditions is related to the heterocoagulation between toner and mineral fillers.

Good flotation of both toner and mineral fillers from MOW can be achieved under the same conditions at pH values between 5.0 and 7.0 for both neutral and alkaline pulping conditions. However, the overall results are significantly improved for the neutral pulping conditions.

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