INTRODUCTION

In modern times, with the ecological concerns about conservation of raw materials and the rapid decline of available landfill space, it has become increasingly necessary to recover and recycle used raw materials. Thus, recovered wastepaper represents a valuable source of raw material for the paper industry. Therefore, the wastepaper must be treated to remove any ink particles and non-ink contaminants (Bridle, 1984). Conventional de-inking is accomplished by converting the wastepaper to pulp and contacting the pulp with an alkaline aqueous de-inking medium containing chemicals that play important roles in the ink separation and removal processes. The physical pulping and the alkalinity of the aqueous medium cause the partial removal of ink from the pulp fiber. The added chemicals complete this removal and produce a suspension and/or dispersion of the ink particles that have been removed from the pulp. The resulting mixture is subsequently treated by flotation or washing to separate the suspended ink from the pulp. Examples of the chemicals used in the conventional de-inking plants include alkali metal hydroxides, alkali metal silicates, oxidative bleaches, and surfactants at temperatures in the range of from 30° to 50°C. Anionic and/or non-ionic surfactants, such as soaps or ethoxylated alkylphenols are mainly used as surface-active agents (Chamblee and Greenwood, 1991).

Much of the previous research on de-inking wastepaper has been directed towards the development of de-inking agents. For instance, Poppel et al. (1986) described a process involving the treatment of the wastepaper in a pulper at an alkaline pH with alkali silicate, an oxidizing bleaching agent, a fatty acid containing more than ten carbon atoms, and a dispersing agent. The acid and dispersing agent are added as an oil-in-water emulsion. Other agents include thiol ethoxylate compounds proposed by Poppel et al. (1986), a mixture of C\textsuperscript{6} to C\textsuperscript{16} alkanols and alcohol ethoxylates suggested by Wood and Fried (1986), or compounds capable of liberating multivalent cations as reported by Wood and Wood (1985). In addition, DeCeuster and Dupriz (1982) used pine oil and a soap-making fatty acid, and a hydrolyzed copolymer.

**Abstract**

This article describes the research leading to the development of a new process for flotation deinking of waste paper, including old newsprint (ONP), magazines, etc. The technique involves a simple reagent scheme (ammonium hydroxide or sodium bicarbonate) that can be used at room temperature to generate fine bubbles at the ink/fiber/water interface that help in the ink particle detachment as well as in rendering ink particles hydrophobic. The reagents also act on desorbing organic species (oil) from oil-based ink, thereby stabilizing the bubbles. A self-aeration flotation machine could be used to enhance flotation kinetics. Experimental studies have been conducted to evaluate different operating conditions, including reagent dosage, flotation time, recycling flotation water, etc. The efficiency of the process is evaluated in terms of yield of clean pulp, brightness, and reagent consumption.

**Key words:** De-inking, Flotation, Ammonium hydroxide, Soda ash.

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Much of the previous research on de-inking wastepaper has been directed towards the development of de-inking agents. For instance, Poppel et al. (1986) described a process involving the treatment of the wastepaper in a pulper at an alkaline pH with alkali silicate, an oxidizing bleaching agent, a fatty acid containing more than ten carbon atoms, and a dispersing agent. The acid and dispersing agent are added as an oil-in-water emulsion. Other agents include thiol ethoxylate compounds proposed by Poppel et al. (1986), a mixture of C\textsuperscript{6} to C\textsuperscript{16} alkanols and alcohol ethoxylates suggested by Wood and Fried (1986), or compounds capable of liberating multivalent cations as reported by Wood and Wood (1985). In addition, DeCeuster and Dupriz (1982) used pine oil and a soap-making fatty acid, and a hydrolyzed copolymer.
Other efforts have addressed washing or flotation methods of separating ink particles from wastepaper fibers (Chamblee, 1991, Dingman, 1999, El-Shall, 2003, Eriksson, 1997, Forsberg, 1994, Haynes, 1998, Miller, 1982, Nanda, 1985, Norman, 1994, Pfalzer, 1981, Renders, 1993, Robertson, 1998, Schwinger, 1994, Shiori, 1988, and Tefft, 1988).

In recent years, however, ink formulations have become more and more complex and involve an increasing use of a wide variety of synthetic resins and plasticizers. Many of the new ink formulations incorporate new pigments, dyes, and toners that are difficult to remove by the conventional aqueous de-inking chemicals. The challenges that the pulp and the paper industry is trying to meet today in the recycling area are to: (1) economically produce quality paper that meets the consumer needs while satisfying legislative demands for the content of recycled paper; and (2) increase the process efficiency in order to facilitate use of recovered paper that currently cannot be processed economically. There exists a need for new recycling processes that are more economical and can handle a wider range of recovered paper. One of the most important steps in recycling the recovered paper is de-inking. There also exists a need for methods of de-inking that can handle (1) a wider variety of printed material (newsprint to high quality glossy magazine paper) and (2) a higher pulp density than the conventional processes.

This paper discloses a new reagent scheme for flotation de-inking of a mixture of old news print (ONP) and old magazine print (OMP). The performance and reagent consumption of the process is discussed in comparison to published data by conventional alkaline process.

MATERIALS AND METHODS

Pulping

The wastepaper, 30% old magazines (OMG) and 70% old news print (ONP), was used in these experiments. The pulp stream is mixed with 0.5—1.0 wt. % hydrogen peroxide and 0.1 wt. % ammonia as ammonium hydroxide or 1—3 wt. % sodium bicarbonate or sodium carbonate. All reagents are related to drypaper weight. The pH in this stage is about 9.5—10.0. The reagents are added during the pulping stage, which is carried out at room temperature in a Hamilton Beach 16 speed blender running at the highest speed for 1—2 minute pulping time at 10% solids by weight (pulp consistency).

Flotation

After pulping, the pulp is then transferred to the flotation machine, which could be a flotation column or a mechanical flotation cell. In this study, a Denver flotation machine (4.0 liter cell) is used. In some tests polypropylene glycol (400 or 4000 molecular weight) was added as a frother. Dosages are indicated in the results section. Unlike the conventional reagent schemes, which can handle only 1.0—1.2% solids loading during flotation, this method can handle up to 2.0% solids loading efficiently. Flotation was done for different times. The froth was collected and periodically scraped off the top of the flotation cell with a small paddle. The ink and pulp deposited on the sides of the cell and the stand pipe were frequently washed down with water. Water was continuously added to keep the froth level constant and at the lip of the cell. This is needed for efficient froth removal. It should be mentioned that the amount of added water was kept as low as possible (about 3—5% of the cell volume) to minimize dilution of the chemicals present in the suspension. Floated ink particles were discarded and pulp left in the cell was separated from the water using 35 mesh screen. The separated water (containing pulping chemicals) was used for testing recycled water. The pulp was then washed on the same screen using fresh water. Fig. 1 shows the flow diagram of the deinking process used in this study.
Preparation of Handsheets

After screening the pulp, vacuum filtration was done using a 15.0 cm diameter funnel under 15 inches of Hg vacuum. A Whatman filter paper No. 40, 15 cm dia., was placed into the funnel to avoid fiber passing through the funnel pores. Another filter paper was placed at the top of the pulp in the funnel. Filtered pulp was pressed between two flat surfaces to form a uniform cake. After pressing, the cake was completely dried in an oven. The mass of dried pulp was used to calculate the yield. Some samples were sent to a specialized lab to measure the ash content before and after de-inking.

Brightness Measurement

The brightness tests were used to measure ink removal. Brightness of formed cake (pad) was measured using hand held Technidyne Technibrite™ TB-1C. The brightness meter was calibrated using calibration plates of known brightness. The brightness readings were averaged of 5 readings for each sample.

RESULTS AND DISCUSSION

In this study, ammonium hydroxide, sodium bicarbonate, and sodium bicarbonate were used in combination with hydrogen peroxide during the pulping stage. Data obtained in these systems are discussed below.

1. Testing Ammonium Hydroxide

Effect of Flotation Time

Effect of flotation time on brightness of pulp is shown in Table 1. The data show that ink floats even after five minutes, as indicated by increasing brightness values of the produced pulp. Extending flotation time to eight minutes improves brightness to a higher value, as shown in Table 1. It is worthy to mention that the (ONP) waste paper (without printing) has a brightness value of 56% The choice of flotation time depends on many factors, including costs (capital and operating), desired quality, and economical yield values.

It is interesting to note that ash content decreases with time, as shown in Fig. 2, indicating that filler particles are also floated with the ink particles. One disadvantage, however, of using longer flotation time is the loss of pulp leading to lower yield values as shown in Fig. 3. The yield decreases markedly when flotation is continued longer than five minutes.

Table 1  Effect of flotation time on brightness of produced pulp (0.5%H₂O₂, 0.1%NH₄OH, 2 minutes pulping)

| Flotation Time, min | Brightness, %ISO |
|---------------------|------------------|
| 1                   | 43               |
| 2                   | 44               |
| 3                   | 49               |
| 4                   | 50               |
| 5                   | 51               |
| 6                   | 54               |
| 8                   | 55.5             |

Fig. 2  Effect of flotation time on ash content of de-inked pulp (0.5%H₂O₂, 0.1%NH₄OH, 2 minutes pulping)

Fig. 3  Effect of flotation time on yield of de-inked pulp (0.5% H₂O₂, 0.1%NH₄OH, 2 minutes pulping)
These results may be attributed to bubble formation due to reactive peroxide and soluble alkaline agents may react in the presence of the pulp that dislodge the ink particles of the fiber and help in floating the ink and filler particles. Using ammonium hydroxide, ammonia gas nucleates at the fiber/solution interface. The reaction may be speculated to proceed according to the following scheme:

$$2\text{NH}_4\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{NH}_3 \uparrow + 2\text{H}_2\text{O} + \text{O} + \text{NH}_4^+ + \text{OH}^-$$

(1)

It should be mentioned that no gas bubbles are observed in absence of pulp. The reasons for activation of such reaction in the presence of pulp are still not clear. Nevertheless, the liberated ammonium gas floats the ink and filler particles to the surface. Hydrogen peroxide bleaches the pulp and contributes to the product brightness. In all results shown below, however, a self-aerated flotation machine was used where air was sparged into the system to enhance flotation kinetics of the filler and ink particles.

Effect of Recycling Process Water

Recycling water for reuse in process industries is important to cost effectiveness of the process as well as reduction of discharge to the environment of possibly contaminated water. Thus, it is important to evaluate the effect of water recycling on the performance of the deinking process and the quality of the deinked pulp. Interestingly, the brightness of the product increases with the number of recycling stages as seen in Fig. 4. It is important also to note that a yield value of 88 ± 1% was obtained in all of these tests. In other words, recycled water does not have detrimental effect on pulp recovery or ink removal.

The brightness improvement may be attributed to two reasons. First is due to the bleaching effect of hydrogen peroxide. Second is stabilization of formed gas bubbles by the released oil due to the action of the hydrogen peroxide. Release of oil is evidenced by a decrease in surface tension of water as shown in Fig. 5. Interestingly, it is found that further decrease in surface tension and increase in total carbon content are obtained by recycling water.

Further testing of this process utilizing higher dosage of reagents and addition of polypropylene glycol with molecular weight of 400 has shown a dramatic improvement in the brightness of deinked pulp. The obtained brightness values for ONP and magazines have reached a level close to original values (Papers without print). These results are discussed in another publication (El-Shall et al. (2003)).

2. Testing Sodium Bicarbonate/Sodium carbonate

Sodium bicarbonate or sodium carbonate was used instead of ammonia in the pulping stage. In these systems, the following reactions may take place:

$$\text{NaHCO}_3 + 2\text{H}_2\text{O}_2 \rightarrow \text{Na}^+ + \text{OH}^- + 2\text{H}_2\text{O} + \text{O}_2 + \text{CO}_2 \uparrow$$

(2)

$$\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}_2 \rightarrow 2\text{Na}^+ + 2\text{OH}^- + 2\text{H}_2\text{O} + \text{O}_2 + \text{O} + \text{CO}_2 \uparrow$$

(3)

The liberated carbon dioxide bubbles would (simi-
lar to the ammonia gas) dislodge the ink particles of the fiber surface and help float them to the surface of the suspension. In this case, the formed molecular oxygen would function as an additional flotation agent.

It is expected that processes utilizing combinations of alkaline agents and peroxides, which do not react with each other to liberate gas bubbles, the process is much less efficient. For example, where alkali metal hydroxides and hydrogen peroxide are utilized, the reagents react according to the scheme:

\[ \text{NaOH} + \text{H}_2\text{O}_2 \rightarrow 2\text{Na}^+\text{OH}^- + \text{H}_2\text{O} + \text{O}_2 \]  

(4)

Although hydrogen peroxide aids in brightening the pulp, no gas bubbles are formed to float the ink particles to the surface of the pulp stream.

In Fig. 6, the experimental data show (as in the case of ammonium hydroxide) the brightness increases as flotation time and reagent dosage increase. It should be mentioned that the flotation time might represent the time needed for the bubbles loaded with ink particles to float. Thus, the type of reagent used may not be of significance during the flotation stage.

On the other hand, the effect of dosage can be explained on the bases of the increased number of fine generated CO$_2$ bubbles, which are responsible for dislodging the ink particles from the fiber surface during the pulping stage.

Most importantly, several tests were conducted using sodium carbonate (less expensive reagent) instead of the bicarbonate. The results indicated that the sodium carbonate could be used to produce a pulp with brightness more than 55% after flotation. Therefore, it may be cost effective to use soda ash instead of ammonia or sodium bicarbonate during the flotation deinking process.

**REAGENT CONSUMPTION AND PERFORMANCE COMPARISONS**

The recommended reagents to be used in this process to produce pulp of high brightness (over 54% for ONP and over 80% for magazines) are listed in **Table 2**. The dosages of these reagents are also listed in the same table together with that used in conventional alkaline pulping as described by Dingman and Perry (1999). The data show that few reagents at lower dosages are used in the developed process. In addition, the process could be more cost effective, especially when a less expensive reagent such as soda ash is used. An added advantage of this process is the high pulp (2%) consistency in flotation as compared to (1.0–1.25% normally used by the industry). This represents over 60% increase in plant capacity. Another important point to remember is that all pulping and flotation are done at room temperature instead of the high temperature conditions (over 40 degrees C) used in conventional de-inking plants (Dingman et al. (1999)).

**Table 2** Comparison between Recipes and Reagent Consumption for Conventional and the Developed Deinking processes

| Process          | Additive                  | Dosage (#/ton) |
|------------------|---------------------------|----------------|
| Conventional Alkaline | Sodium hydroxide           | 12             |
|                  | Hydrogen peroxide         | 16             |
|                  | Chelant                   | 4              |
|                  | Sodium silicate           | 20             |
| UF Process-1     | Hydrogen peroxide         | 20             |
|                  | Ammonium hydroxide        | 4              |
|                  | PPG                       | 0.5            |
| UF Process-2     | Hydrogen peroxide         | 10             |
|                  | Sodium carbonate          | 10             |
|                  | PPG (400 MW)              | 0.5            |

**CONCLUSIONS**

A simple and effective deinking process involving pulping and flotation steps was developed. The process depends on adding reagents in the pulping stage that lead to formation of fine bubbles at
ink/fiber/water interface. The results of preliminary tests showed that brightness more than 55% could be obtained from a mixed stock containing 30% old magazines (OMP) and 70% old newsprint (ONP). The process has several features such as, few chemicals such as hydrogen peroxide and Alkali reagent (e.g., Ammonium hydroxide, Sodium bicarbonate and sodium carbonate) are used, and high yield of good quality (brightness) product. From a practical and economic view points, this process may prove to be more economical due to low reagent's consumption, operating at room temperature, increased plant capacity by floating higher solid content pulp, and possibility of water recycling. Further testing at larger scale is recommended to verify the potential of this process.

Acknowledgement

Financial support from the following institutions is acknowledged and greatly appreciated: the Particle Engineering Research Center (PERC) at the University of Florida; the National Science Foundation (NSF), under grant EEC-94-02989; and the Industrial Partners of the ERC.

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