Upgrading Recovered Paper With Enzyme Pretreatment and Pressurized Peroxide Bleaching

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ABSTRACT

Enzyme pretreatments, shown to be effective for toner ink removal, can improve the bleachability of low quality recovered paper. When followed by pressurized peroxide bleaching, enzyme pretreated pulps display a higher level of brightness and are substantially cleaner than conventionally deinked control pulps. In this study, experiments using low quality mixed recovered paper demonstrated that an enzymatic pretreatment improves the removal of residual inks and aids in bleaching mechanical and unbleached fibers which are major contaminants in recycled furnish. Preliminary investigation also suggests a slightly improved brightness stability of bleached enzyme pretreated pulp, an important advantage for pulps containing mechanical fibers. Enzymatic pretreatments could play a significant role in upgrading residential recovered paper pulp.

KEYWORDS

Bleaching, Deinking, Enzymes, Peroxide, Recovered fiber, Waste papers

INTRODUCTION

Economics, conservation policies, and mandated recycled-content regulations have combined to make the recycling of recovered paper a rapidly growing segment of the pulp and paper industry. It is projected that 50% (about 45 x 10^6 tons/year) recovery will be realized by the year 2000. Newly built recycling mills competing for quality recovered paper have dramatically affected the business of paper recycling. The current situation indicates that mills will have to depend on a more heterogeneous, lower quality paper source. However, recycling typical residential or mixed office waste (MOW) is not simple. The need to utilize lower quality recovered paper has shifted the focus of recycling from deinking to bleaching, color stripping, brightness stability, and contaminant removal. Existing technologies need to be modified to achieve more effective recycling.

Research has demonstrated that toner inks, a major contaminant remaining in deinked market pulps, can be substantially removed with commercially available enzyme preparations (1). The effectiveness of enzymes for toner removal was subsequently confirmed on an industrial scale (2,3). In addition to efficient, cost-effective ink removal, enzyme deinking results in increased pulp brightness (1,2,3). Several points of additional pulp brightness achieved during deinking translates into a reduced bleaching requirement to meet a target brightness. Bleach-chemical reduction has implicit economic and environmental advantages. Paired with other demonstrated advantages of using enzymes in repulping recovered paper, increased freeness and papermachine runnability, improved bleachability could permit papermakers to utilize lower quality mixed recovered paper to produce a high brightness bleached pulp.

This paper focuses on two critical aspects of recycling typical residential recovered paper: initial paper processing and bleaching. Because bleaching depends on as clean of furnish as possible, the cleaning, screening, and deinking sequences used on this furnish are presented first. Next, a promising, novel approach to bleaching low quality recovered paper is discussed. This bleaching process uses hydrogen peroxide under low oxygen pressure maintained in a high consistency refiner. A comparison is made with similar peroxide bleaching carried out at medium consistency under conventional atmospheric conditions. Finally, optical properties, cleanliness

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of the bleached pulps, and brightness stability are presented.

EXPERIMENTAL

Paper Furnish

The paper selected for this study was a typical residential curbside mix excluding nonpaper items. Newspapers (ONP) and magazines (OMG) comprised approximately half of this furnish. The remaining furnish contained mixed paper, including junk mail, mixed office papers with high color content, and minimal unbleached kraft.

Cleaning/Screening/Washing

Recovered paper was pulped at ambient pH for 20 min at 4% consistency with soft 50° C water, screened through 0.210-mm slots at 1% consistency prior to processing through 7.62-cm forward cleaners and throughflow cleaners at 0.75% consistency. Cleaned pulp was floated at 1% consistency using 0.2% nonionic surfactant on oven-dried (o.d.) pulp, washed on a 70-mesh sidehill screen washer, and dewatered on a press to approximately 30% solids.

Enzyme Treatment

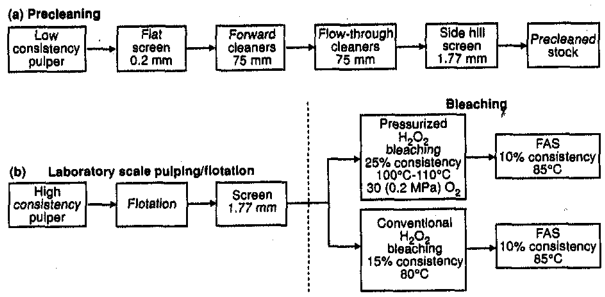
Bench-scale experiments used 250 g (o.d.) cleaned pulp for medium (14%) consistency pretreatment in a jacketed Hobart[1] mixer for 30 min at 55° C. Enzyme trials incorporated 0.04% Novozym 342 (Novo Nordisk BioChem) concentrate and 0.10% nonionic surfactant based on o.d. pulp, according to procedures previously established for deinking trials in our laboratory (1). Novozym 342 is a neutral cellulase preparation, additionally displaying xylanase, mannanase, and other enzymatic activities. Pulps were subsequently floated for 5 min, drained over a sidehill screen washer, washed, and pressed to 30% solids. An identical protocol was used for the control (without enzyme) runs except that water was substituted for enzyme preparation.

Bleaching

Conventional hydrogen peroxide bleaching was done on 20 g (o.d. basis) cleaned pulp chelated with 0.5% DTPA. The bleach formulation, based on

[1]The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

Figure 1: **(a) Precleaning process sequence (b) pulping with or without enzyme preparation, flotation, and alternate bleaching sequences for precleaned furnish.**



charge by weight of o.d. pulp, included 2% hydrogen peroxide, 3% sodium silicate, 0.5% magnesium sulfate, and 1.2% sodium hydroxide. Bleach conditions used were 15% solids, 90 min, 80° C. Bleached pulp was neutralized to pH 6 with sodium bisulfite and washed thoroughly.

For the pressurized peroxide (PO) bleach sequence, 500 g (o.d.) batches of precleaned pulp were run with and without enzyme pretreatment. Hydrogen peroxide and stabilizing chemicals were mixed into the pulp at high (25%) consistency. Bleaching was carried out in a pressurized refiner. Pulp was added to the holding chamber of the batch refiner. Oxygen was injected into the presteamed holding chamber to achieve 0.2 MPa, which was the sealed pressure limit of the equipment used. Pressure was maintained in the sealed chamber for approximately 15 min at about 100° C to 110° C before being fed by auger to refiner plates set at a wide gap (approximately 5.0 mm) setting to avoid a dispersion effect on the pulp. Bleached pulp was thoroughly washed and neutralized to remove bleach residuals. Handsheets were made for both conventional and PO bleached pulps according to TAPPI T-205 for examination of optical properties.

Reductive bleaching with formamidine sulfinic acid (FAS) was done on 20 g samples of peroxide-bleached pulps. Conditions used were 10% consistency, 85° C, 45 min at initial pH about 10. Chemical charge was 1% FAS and 0.6% NaOH. Bleached pulp was washed thoroughly and made into 3 g sheets for brightness measurements, according to TAPPI T-525 om-92 using a Technidyne brightness meter.

Other Measurements

Ash in the pulp was determined at 525° C, and kappa numbers were measured on original stock from the pulper, after the cleaning process, and after PO bleaching. Residual ink in the 0.02 to 4.0 mm^2 range was counted on 1.2 g handsheets by image analysis with an Optomax Speck Check scanner at 125 detection level, resolution of 400 dots per inch, no shade compensation. Tensile and burst indices were measured using TAPPI T-494 and T-403, respectively. Post color numbers were calculated according to TAPPI TIS-0606-18.

RESULTS AND DISCUSSION

Paper Processing

By definition, low quality recovered paper implies heterogeneity of paper stock, printing inks, contaminants, and papermaking additives. The paper furnish used for this study had an initial kappa number 42, GE brightness 47.5%, b* +5.6, 8.2% ash. Because of the complexity of this paper furnish, we found it essential to clean and screen the recovered paper prior to application of enzyme preparations or bleach chemicals (Fig. 1a), We found that both processes are more responsive when ash, water-dispersible inks, and other contaminants have been removed. Removal of water dispersible inks, fillers, and some fines increased the brightness of the furnish to 56.7% GE, +6.1 b* values, and reduced the ash content to 2%. The dirt count of the precleaned stock was still very high; 1,172 ppm prior to enzyme treatment (Table 2).

Previously, our enzyme deinking experiments used high brightness, 100% toner-printed office papers. This homogeneous high quality paper furnish was successfully deinked using the repulping and flotation sequence illustrated in Fig. 1b, and bleached if required. However, for the low quality furnish used in this study, precleaning preceded medium consistency repulping with or without active enzyme preparation (Fig. 1b). Table 1 summarizes the change in ash, brightness, and kappa number of this paper furnish at various stages of processing.

Pretreatment and Bleaching

Enzyme treatment

Enzyme treatment of the cleaned pulp builds on improved contaminant removal to increase bleachability with conventional oxidative and reductive bleach chemicals. Residual ink present in the cleaned pulp was removed by medium consistency enzymatic treatment followed by flotation. Our results demonstrate that the enzyme treatment makes the subsequent bleaching of this furnish more effective. In Fig. 2, we show that with enzyme pretreatment, GE brightness of 80% was achieved using a POY_{FAS} bleach sequence. Brightness of the bleached control (without the enzyme treatment) was approximately 77% GE. Multiple replicates were run. The values reported here are representative of the bleach response for this furnish.

Prior to these experiments, we had seen a brightness increase with enzyme treatments during an industrial evaluation of enzyme-enhanced toner removal (2). In those trials, the control using a heat-deactivated enzyme preparation resulted in a final deinked pulp brightness of 82.2% GE, an increase of 7.9% GE over the flotation feed brightness of 74.3% GE. Two similar trials using an active en-

Table 1. Kappa, Ash, Brightness, and b* Values of Residential Recovered Paper at Various Stages of Cleaning and Bleaching.

Stage	Kappa number	Ash %	Brightness %	color b*
Initial	42	8.2	47.5	5.6
After cleaning	42	~ 2	55.8	6.2

Table 2. TAPPI Dirt Counht Before and After Pressurized Peroxide (PO) Bleaching, With or Without Enzyme Treatment.

	Residual ink (ppm)
After precleaning	1172
After PO bleaching	
Control	128
Enzume treated	35

[1]0.02-4.0 mm^2; 125 detection level counted on Optomax Speck Check.

Table 3. Burst and Tensile Indices of Residential Recovered Paper Treated With or Without Enzymes, Before and After Pressurized Peroxide (PO) Bleaching.

	Burst indexs (kP·m²/g)	Tensile index (kN·m/g)
Bdfore PO		
Control	1.87	34.3
Enzyme	1.86	34.9
After PO		
Control	2.27	38.2
Enzyme	2.18	39.1

zyme preparation resulted in 75.8/85.7% GE and 77.2/86.2% GE for the respective flotation feeds/final brightness. This was equivalent to 9.9% and 9.0% GE brightness increase, respectively. Because the deinked brightness was already high, no bleaching was required.

The commercially available neutral cellulase preparation used for toner removal also contains a mixture of hemicellulases (4), which may facilitate subsequent bleaching of this high lignin-containing pulp. Xylanase has been extensively investigated for prebleaching kraft pulp to minimize chlorine demand required for high brightness (5-7). Recently, researchers have examined enhancing peroxide, oxygen, or a combination of both bleach sequences on virgin kraft pulps with xylanase pretreatments (8). It is generally accepted that residual lignin covalently bonded to hemicellulose in the cell wall can be accessed by enzymatic hydrolysis. The role of the hemicellulases in the prebleaching stage is to weaken or break these bonds that, in turn, facilitate delignification during subsequent bleaching (6, 9, 10). The large quantity of high lignin-content fibers in low quality recovered paper creates a similar opportunity for enzymatic pretreatment for recycled fiber. It is possible that the hemicellulase components of the enzyme blend we used in this study increased fiber porosity that improves accessibility of bleach chemicals.

Table 4. Brightness Reversion[1] of Aged POY_{FAS} Bleached Recovered Paper, With or Without Enzyme Pretreatment.

	Thermal aging (105°C)		Photo aging (300-400 nm)	
	24 hr	48 hr	30minh	90 min
Control	2.66	7.19	4.39	4.87
Enzyme	2.39	5.95	3.67	4.66

[1]Reversion is expressed in post color numbers.

Bleaching

Initially, we used conventional 2% hydrogen peroxide at medium consistency to brighten the deinked pulp. Bleach response was limited to approximately 9 brightness points, bringing the brightness of the furnish up to only 66% GE. It was clear that a more powerful bleaching agent was required to deal with this recovered paper. We found that pressurizing the peroxide with oxygen resulted in a substantial improvement in brightness (Fig. 2).

The additional advantage of enzyme pretreatment was clearly demonstrated when deinked pulps were bleached with hydrogen peroxide pressurized with oxygen. Not only was brightness increased, but the pulp was also substantially cleaner (Fig. 3). The enzyme treatment also appeared to more effectively brighten unbleached fibers and remove residual ink specks and other contaminants. It is difficult to quantify residual contaminants, such as dyed or unbleached fibers, on handsheets. However, residual ink scanned by image analysis indicates relative contaminant removal. Results indicated 35 ppm dirt in the enzyme treated pulp vs. 128 ppm dirt in the control (Table 2).

Pressurized peroxide (PO) is an emerging bleach technology used in TCF (totally chlorine free) bleaching of virgin chemical pulps to achieve high levels of brightness. Usually, simultaneous side reactions that occur during peroxide bleaching detract from the production of the perhydroxyl anion (OOH) believed to be responsible for chromophore oxidation. Formation of this active bleach anion can be accelerated by increasing the peroxide or alkali concentrations or increasing temperature. Unfortunately, higher temperatures also contribute to the instability of peroxide. However, increased pressure permits the use of high temperature to accelerate perhydroxyl ion formation while inhibiting negative side reactions (11,12) , pressure improves the

Figure 2: **Bleaching response of recovered paper with H_2O_2, PO, and FAS at various stages of cleaning when pulped with or without enzyme preparation. A is initial paper furnish, B is response after screening and cleaning, C and D are responses after screening, cleaning, and washing.**

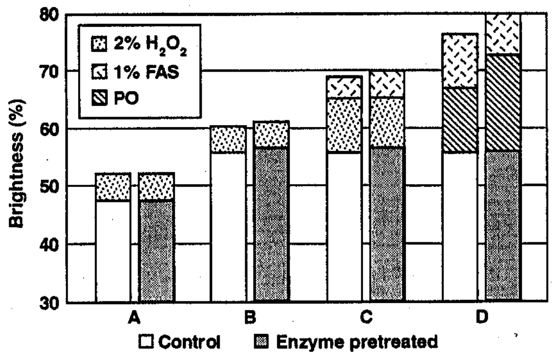
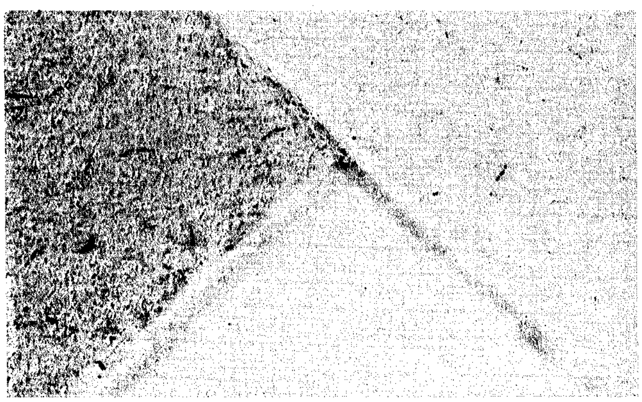


Figure 3: **Cleanliness of enzyme deinked residential paper (upper left), after conventional H_2O_2 bleaching (upper right), and after PO bleaching (bottom).**



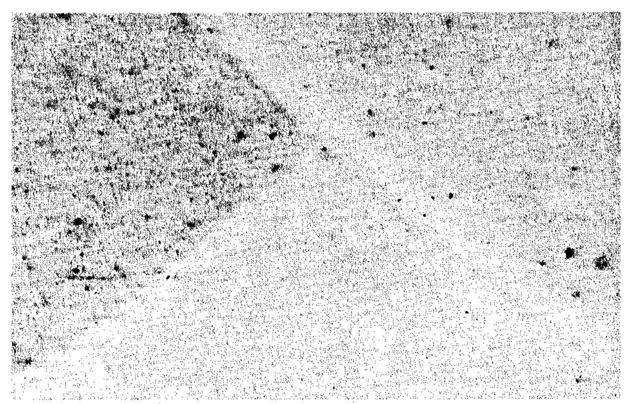
efficiency of peroxide bleaching, thus permitting either a higher end brightness or reduced chemical consumption for a comparable peroxide charge.

In contrast, conventional oxygen bleaching requires specialized equipment to maintain 0.4 to 0.7 MPa for 1 to 2 hr to accomplish delignification. Apparently, only relatively low pressure is required to deter competitive side reactions that decompose peroxide in PO bleaching (12). A lower pressure requirement permits the use of equipment currently in place in recycling facilities; higher temperature shortens the retention time, thereby facilitating production. Lower pressure and shortened retention time contribute significantly to preserving recovered fiber yield. Although increased pressure or longer retention time might produce an even cleaner pulp, incorporation of an enzyme pretreatment stage produces an impressively clean pulp under the conditions used for this study.

Typically, bleaching of recycled fiber requires both oxidative and reductive bleaching; oxidative bleaching for brightness improvement and reductive bleaching for color removal (13). Sodium hydrosulfite and FAS are the most common reductive chemicals. A high charge of FAS as a second stage bleach was used in this study. The response was noteworthy (Fig. 2), adding as much as 9 brightness points as well as decreasing the b* value.

Papermakers hesitate to accept more than 10% mechanical fiber content in recovered paper furnishes intended for printing and writing grades. However, because the lignin content varies considerably in softwood and hardwoods, the actual percentage of lignin contained within that upper limit is also variable. The primary concerns about the presence of high mechanical fiber content are pulp

Figure 4: **Cleanliness of bleached/unbleached recovered fiber mixture (upper left), after PO bleaching without enzyme treatment (upperright), and with enzyme treatment (bottom).**



yield and optimum achievable bleached brightness. Lachenal (14) has explained that final bleached brightness is limited to the optimum brightness of mechanical pulps, if more than 30% of a furnish is composed of mechanical fiber. The recovered paper used in this study contained at least 35% mechanical fiber, which may explain why the best bleached brightness achieved on this furnish was 80%. Yield was not measured on all of these bleaching trials. However, on several runs that were measured, yields were 92-94% of the cleaned furnish. Kappa numbers measured on various runs showed a decrease from 42 to 36 after PO bleaching, which indicates loss through delignification. Fiber strength was maintained on both the control and enzyme pretreated pulps during PO bleaching (Table 3).

A question not specifically answered from our experiments on residential mixed recovered paper was whether unbleached fibers could be selectively bleached. Therefore, we put together a batch of unprinted copy paper and added approximately 1% unbleached kraft fibers and 5% laser-printed computer printout paper. The initial brightness of this batch was 69.3%. This paper was pulped with and without enzyme and both batches were bleached with PO. The enzyme pretreated pulp reached a PO brightness of 84.1%, while the control pulp approached 80.0%. More important than brightness is the dramatic difference in cleanliness as illustrated in a photograph taken under a light microscope (Fig. 4). The enzyme pretreated pulp is virtually free of residual ink and unbleached fibers, whereas these contaminants are still visible on the control that was pulped without the enzyme preparation.

Another factor that needs consideration when attempting to upgrade low quality recovered paper is brightness stability. Although some delignification occurs during bleaching, removal of too much lignin at this point will cause a sacrifice in yield. Implicit in bleaching high lignin content pulp is color reversion, yellowing over time. Preliminary examination of brightness stability of this residential recovered paper bleached with pressurized peroxide suggests that enzyme pretreatment may also inhibit the rate of brightness reversion (Table 4). Additional data are needed to confirm this observation, however, delaying reversion is a promising possibility consistent with findings of other researchers (15).

Papermakers realize that in order to use low grade recovered paper, multistage processing of paper is essential (16). As the quality of the furnish decreases, processing necessarily increases both in cleaning and bleaching. New recycling mills include additional flotation and bleaching stages to handle more heterogeneous furnishes. In October 1995, American Fiber Resources opened a recycled market pulp mill in Sanford, West Virginia. Under the heading of "Taking pulp into the next generation,'' the author describes a "different" and "daring" deinked market pulp producer that includes a PO stage in the processing of low quality recovered paper to high brightness (17). Although specifics on the PO stage are not presented, the overview appears to be compatible with requirements for enzyme deinking that we used in our experimental work. Paired with enzymatic pretreatment, the PO stage presently in place might permit 100% postconsumer recovered paper to be successfully reprocessed into deinked pulp.

CONCLUSIONS

Efforts to recycle residential recovered paper benefit from deinking processes that remove both water soluble inks (washing) and toner inks (flotation) followed by sequential oxidative and reductive bleaching.

Enzyme treatment of cleaned, low quality recovered fiber results in improved bleachability and contaminant removal.

High lignin-containing residential recovered paper is responsive to pressurized peroxide bleaching.

Enzyme treatments followed by pressurized peroxide bleaching significantly improve pulp brightness and aid the brightness stability of unbleached and mechanical fibers in low quality recovered paper.

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