RECYCLING BLEACH TECHNOLOGIES

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ABSTRACT

When faced with bleaching recycled fibers, the technologist must consider the usual factors associated with the bleaching of virgin fibers plus additional factors introduced by recycling. The lignin content of the furnish and the products to be made determine whether delignifying or lignin-preserving agents are to be used. Factors introduced by recycling include mixed lignin contents, dyes, residual ink particles and carrier chemicals, contaminants, color reversion, and hornification (which affects accessibility of chromophores to bleaching reagents). In addition, the technologist must be concerned with the environmental impact of the bleaching operation.

Dithionite and formamidine sulfonic acid are effective lignin-preserving reductive bleaching agents for recycled fibers. Hydrogen peroxide is an effective lignin-preserving oxidative agent, but heavy metals and enzymes catalyze its decomposition. Chelating agents have an important role in decreasing metal content. For some delignification and effective removal of organic chromophores, oxygen and ozone show promise. Research on the use of oxygen-based oxidative bleaching agents is intense because of their favorable environmental attributes.

OVERVIEW

The production and consumption of paper and paper products add new dimensions to the bleaching of wood pulp fibers. Although many underlying principles and chemicals are the same for recycled or virgin fiber bleaching, additional problems and research opportunities are presented by increasing the use of recycled fibers. The primary distinction in bleaching virgin fibers is whether the fibers contain most of the original lignin, as do mechanical- and chemimechanical-type pulps, or whether most of the lignin has been removed by chemical pulping and the remaining lignin is removed in the bleaching operation. This is also a major consideration in bleaching recycled fibers, but in the case of the latter, virgin and recycled fibers are often mixed.

Reagents used to bleach or “brighten” high-yield pulps (high lignin content retained after bleaching) are milder in their action than reagents used for delignification. Both mild oxidative and reductive treatments are effective; the most commonly used reagents are hydrogen (sodium) peroxide and sodium dithionite (hydrosulfite). When delignification is required, the reagents used include chlorine and chlorine-oxygen compounds, oxygen, and ozone. For the purposes of this discussion, the bleaching treatment will be categorized by function as delignifying or brightening. A third bleaching function, unique to recycled papers, is the color stripping of dyes.

Constraints imposed on virgin fiber bleaching affect the bleaching of recycled fibers as well. The major constraints are environmental, economic, and technical. Pulp bleaching is currently in a state of rapid change because of the environmental issues of by-product generation of chlorinated dioxins and chlorinated benzofurans from chlorine bleaching and chloroform generation from hypochlorite bleaching. Both chlorine and hypochlorite are presently used in the bleaching of recycled papers. Economically, the bleaching stage by itself does not contribute much to profit. Bleaching is performed as a matter of necessity to obtain the properties required of the particular product. Also, the scale of paper production and low unit price create continual pressure to bleach as efficiently and inexpensively as possible. The main technical constraint on bleaching arises from the fact
that color bodies are a small fraction of the pulp mass. Chemical reagents that bleach must be highly selective. If the carbohydrates that compose the bulk of the fiber mass are attacked, the physical properties of the paper product will suffer. If lignin is attacked unnecessarily, there will be excessive chemical consumption and loss of fiber yield.

Certain considerate ions apply specifically to post consumer waste papers. Such papers often contain a mixture of mechanical and chemical pulps even if postconsumer separation is employed because the paper products may use a blend of the two types of pulps. Such mixtures are difficult to bleach homogeneously and effectively without overbleaching the chemical pulps. Unfortunately, this mixture problem is anticipated to increase as the extent of recycling increases and separation becomes more difficult. Another major consideration is whether the recycled papers have been dyed. Other factors such as the printing processes and ink types used on the papers affect bleaching efficiency, but they are less of a consideration in choosing a bleaching method. In practice, the efficiency of the deinking operation has a large impact on the bleaching stage [1]. However, for our purposes, it is assumed that deinking is performed with maximum efficiency. After exposure to light and varying atmospheric conditions, white papers undergo color reversion. This is true particularly for the high-yield lignin-containing pulps, but less so for fully bleached chemical pulps. The reverted color is considered somewhat more difficult to bleach than the original color [2].

Because of the extreme variability of the recycled paper supply, it is generally recommended that each mill perform optimization studies for its own supply of recycled paper. The results of many laboratory empirical studies have been published and more are continuously appearing. These results should provide a guide to selecting the best processes to be optimized. Process control is more difficult with recycled fibers than with virgin fibers. Sensors based on the principle of oxidation-reduction potentials (ORP) appear to give satisfactory results [3].

This report concentrates on the principles of bleaching recycled fibers to the extent that such principles can be generalized. Operating conditions are not discussed.

**BRIGHTENING**

Brightening and lignin-preserving bleaching are terms used to describe the bleaching of pulps that contain most of the original wood lignin. The goal is to achieve sufficient brightness for the end product, which is usually newsprint or another short-life product for which permanent brightness is not important. However, the trend is to use the less expensive high-yield pulps wherever possible, and considerable research effort has been expended to find ways to stabilize the brightness of these pulps. Lignin is retained in the pulp primarily for yield, but lignin is generally considered to be susceptible to “yellowing” or “brightness reversion.” With bleached chemical pulps, functional groups in the carbohydrates that may have been introduced during processing are considered the source of yellowing [4].

The original chromophores in mechanical pulps arise primarily from a group of compounds broadly classified as extraneous materials. These nonstructural components are rather species-specific, but they encompass such organic compounds as flavonoids, polyphenolics, tannins, resins, and fatty acids. The compounds may be colored or may form colored complexes with iron or other metals present in the wood or picked up during processing. The heartwood of most woods is darker than the sapwood because of the higher content of extraneous material. Recycled mechanical pulp that was previously brightened loses some brightness because of the regeneration of chromophoric groups. Specific functional groups contributing to color are carbonyl and unsaturated carbon-carbon bonds, which are susceptible to oxidation and reduction. “Alkali-yellowing,” common to most mechanical pulps, is undoubtedly caused by phenolic, enolic, and carboxylic groups that, upon ionization, extend the chromophoric conjugation system.
**Hydrogen Peroxide**

Hydrogen peroxide or its sodium salt is a commonly used lignin-preserving brightening agent. The advantages of hydrogen peroxide are excellent environment compatibility, effectiveness under alkaline conditions, and unprohibitive cost. The major disadvantage is rapid decomposition, which is very subject to trace metal or enzyme catalysis. The enzymes are denatured by heat or hypochlorite treatment, and metals must be deactivated or removed by additional chemicals such as chelants, acid treatments, silicates, and magnesium salts used individually or, more commonly, in combination. Hydrogen peroxide bleaching effluents may have a higher biological oxygen demand load than those from reductive agents. In addition, the extent of brightening that can be achieved by hydrogen peroxide alone is limited.

Hydrogen peroxide may be added at the repulping stage because it is active at the alkaline pH commonly employed [5]. However, the metal ion content is high at that point, and excess chelating capacity is necessary to prevent metal-catalyzed decomposition of the peroxide. Hydrogen peroxide is added at this stage mainly to maintain brightness and prevent alkali yellowing. It may be carried over to the deinking stage. Sodium silicate is commonly used in conjunction with hydrogen peroxide bleaching. Its function is at least three-fold: it buffers the alkaline pH of the system, it provides a source of alkali, and it deactivates metal ions. Organic chelants are also used. Diethylenetriaminepentaacetic acid (DTPA) and diethylenetriaminepenta(methylene phosphoric acid) (DTPMPA) are two chelants that have been shown to be effective [5]. One change in processing that improves the effectiveness of hydrogen peroxide added at the pulper stage is to raise the consistency of the pulp slurry. The effective concentration of the hydrogen peroxide is thereby increased and the amount of metal ions is decreased by removal with the thickening filtrate. Hydrogen peroxide is effectively employed in a separate bleaching stage after deinking. Again, a high consistency is favorable and buffers and chelants are useful.

**Dithionite**

At least part of the various chromophoric systems is subject to either oxidation or reduction. The divalent anion $S_2O_4^2-$ (the preferred term is dithionite, but this anion is also called hydrosulfite, especially in the older literature) is an inexpensive yet effective reducing agent that has long been employed to brighten mechanical pulps. The oxidation products are sulfite or sulfate, which are considered to be environmentally benign. Reducing agents do not adversely affect the pulp strength properties as oxidizing agents may, and therefore the conditions of application need not be as strictly controlled. Optimum bleaching results are usually obtained near neutral pH’s, but dithionite has been used under highly alkaline conditions. Acid conditions below pH 4 decompose the reagent. A single bleaching stage with dithionite may be sufficient to brighten the recycled fiber for use in newsprint, but it does not prevent alkali yellowing as does peroxide.

Sodium borohydride is an efficient reducing agent, but it is generally too expensive to be cost effective. Thiourea dioxide or formamidine sulfinic acid (FAS) is a reducing agent that shows promise in use with recycled fibers. The products from reduction with FAS are urea and sulfate. This reagent is especially effective for color stripping.

**Combined Brightening Stages**

Often the desired brightness is higher than can be obtained in a single stage with either an oxidative or a reducing agent alone. If hydrogen peroxide is used in the pulping or deinking stage and alkali yellowing is avoided, a single subsequent reductive bleaching stage with dithionite may be sufficient. A two-stage “post bleaching” with hydrogen peroxide followed by dithionite or FAS may be used for high brightness. Obviously, the chemicals in the two stages are incompatible, and residual peroxide must be washed out or destroyed before the reductive stage. Dithionite is even subject to air oxidation. The sequence of oxidant followed by reductant is usually recommended because the effects of reduction of chromophores are more easily reversed than are those of oxidation [6].
However, in at least one case [7], bleaching with FAS followed by hydrogen peroxide resulted in significantly better brightness than if the order was reversed.

COLOR STRIPPING

The bleaching of colored papers is a separate problem. Much color is often removed in the deinking step, especially if colored inks or pigments are only physically entrapped in the fiber matrix. However, many dyes Armstrong adsorbed onto the fibers and are resistant to deinking and to mild oxidative treatment, such as hydrogen peroxide, Hypochlorite and chlorine are often effective in destroying dyestuffs, but their use may not continue.

More than 300,000 color agents are reported in use [8]. Fortunately, the number in common use in papers is much smaller, and classes of dyes have similar chemical characteristics. It is very helpful to know the nature of the dye being bleached. Dyes can be classified in several ways. The most common way is to classify dyes as basic, acidic, or direct (substantive). Basic dyes, which have been used for unbleached pulps and groundwood because of their attachment to lignin, are falling into disfavor because of suspected carcinogenicity. This class includes dyes such as Rhodamine, Victoria Green, and Victoria Blue. The acid dyes have a high volatility and include dyes such as Quinoline Yellow and Orange Il. The acid dyes require the use of size and alum to bind to paper.

The most frequently used dyes in the paper industry are the direct dyes. The direct dyes are similar to acid dyes but are of higher molecular weight and do not require separate bonding agents. The direct dyes are the sodium salts of dye acids and bond to cellulose through hydrogen bonding of separate functional groups. At least two such functional groups per molecule are necessary. The majority of the direct dyes are azo dyes. The class also includes stilbene, phthalocyanine, and dioazine, and some anthraquinonine-, quinoline-, and thiazole-type dyes. Many direct dyes used in papermaking can be decolored with reductive bleaching agents. The azo linkage is susceptible to reduction and frequently gives colorless products. However, many of the reduced amine compounds have a yellowish color that must be destroyed by oxidative bleaching agents. The smaller molecules from the reduced direct dyes are more likely to affect aquatic life, and many aromatic amines are suspected carcinogens. Therefore, their further destruction in waste streams is desirable. Current research is developing nonmutagenic dye intermediates [9]. If the amines used in azo dye production are not genotoxic, the reduction products of the dyes will be safe.

A new class of direct dyes, designed to increase water solubility for application and overcome the electronegative repulsion of cellulose, is the cationic direct dye. The charged functional group is located away from the chromophoric functional center. Upon reduction of the chromophoric group, a smaller water-insoluble fragment and a charged, water-soluble fragment may result. Some insoluble fragments may retain a slight yellow color.

The acid anthraquinone dyes are problematic because reduction to hydroquinones results in a yellow or brown color and the dyes are easily deoxidized to the quinone state. The ionic hydroquinone state is more water-soluble and the dyes are then amenable to removal by washing before they are reoxidized to the quinones. Fiber-reactive dyes, which are covalently bonded, are very difficult to remove and they often also contain a quinone function.

In 1962, Barton published a very useful report on the decolonization of dyed paper stock with zinc hydrosulfite [10]. Although the zinc salt is no longer used for environmental reasons, the results of this study should be equally applicable to sodium dithionite. Barton used the chemical classification of the Colour Index number system [11] combined with the known analytical reactivity of many dyes with dithionite to give a scheme to estimate the stripping characteristics of most identifiable dyes. He concluded that dithionite can effectively color strip dyes with color index numbers less than 41,000. These include nitroso-nitro and azo dyes. Some dyes with higher index numbers are also reduceable with dithionite. Dithionite could destroy 66 percent of the acid, 12 percent of the basic, and 98 percent of the direct dyes listed by the American Dye Manufacturers at that time. A more recent paper from Germany gives the bleachability of different colors using various bleaching conditions [12].
Preliminary mill trials and laboratory data indicate that many dyes can be more effectively stripped with FAS than dithionite. FAS is effective at alkaline pH’s and thus may be a replacement for hypochlorite. Current information from U.S. suppliers [13] indicates that approximately 70 to 80 percent of the dyes currently in use can be stripped with FAS compared with about 50 percent that can be removed with sodium dithionite. Examples of the relative color stripping ability of FAS and dithionite have recently been reported [14,15].

Ozone is beginning to be commercially applied as a replacement for chlorine in pulp bleaching [16]. In an investigation of potential bleaching agents for anticipated mixes of secondary fiber, ozone could be used to effectively strip the color from multicolored ledger [17]. Other researchers have also noted the effective color-stripping ability of ozone [18,19].

So far, we have used the term brightness to indicate the degree of bleaching or approach toward “whiteness.” In the paper industry, brightness is defined as the diffuse reflectance of light of 457 nm wavelength. This is not necessarily a measure of the appearance of the paper to the human eye. In some cases, customers specify that the recycled pulp meet other color criteria. The International Commission on Illumination (CIE) 1976 L*a*b* system is commonly accepted for determining the calorimetry of white and near-white paper and paperboard [see 20, 21 (references therein)]. The determinations of L*, a*, and b* describe the color spectrum numerically as a three-dimensional “color space.” L* represents lightness from black to white, a* represents green to red as negative to positive, and b* represents blue to yellow as negative to positive. The results of this system correlate well with normal visual judgments of color appearance.

DELIGNIFICATION

Delignification during bleaching is generally an undesirable but necessary operation to obtain a bright product with low color reversion and good permanence. In the original chemical pulping systems, the delignification by pulping reagents must be stopped while a portion of lignin remains in the fiber; the harsh pulping conditions lead to strength losses beyond a certain optimum extent of pulping. Delignification is then continued in the milder bleaching stages. In recycling, the lignin coming into the system is usually from mechanical fibers; the amounts of lignin vary considerably, depending on the source and particular mix of recycled stock. Even more challenging is to delignify high lignin content fibers without damaging the fibers from which lignin has already been removed. If too much delignification occurs in the mixture, there is a loss in yield and excessive consumption of chemicals.

Chlorine is a mild, effective, and inexpensive delignifying agent, especially if followed by an alkali extraction stage to continue lignin depolymerization and solubilize the partially oxidized, partially substituted lignin. In recycled fiber, chlorine also has the advantage of reacting with many dyes. Unfortunately, small amounts of chlorinated dioxins and chlorinated benzofurans are produced in the reactions of chlorine with lignin, and these substances undoubtedly would be formed in reactions with the often-uncharacterized contaminants in recycled papers. Chlorine is being replaced by other bleaching agents to meet environmental regulations, but other research is directed toward retaining chlorine while eliminating the release of chlorinated dioxins. This may be accomplished by process modifications, such as sequential addition of chlorine, or by recycling chlorine effluents [22].

Hypochlorite is also an effective, economical bleaching agent, but it has the undesirable attribute of generating chloroform through the haloform reaction. Hypochlorite has a greater tendency to damage fibers through cellulose depolymerization than does chlorine. Also, the reaction of alkaline hypochlorite with mechanical pulps produces a yellow color, which strictly limits the percentage of mechanical pulp that can be tolerated in a stock to be bleached with hypochlorite. Because of its oxidizing power and good dye stripping abilities, a one-stage hypochlorite treatment of many recycled paper furnish is sufficient to provide the desired bleaching.
The two major reagents under study as potential chlorine and hypochlorite replacements in recycled pulp bleaching are oxygen and ozone. Oxygen gas is applied under alkaline conditions, sometimes as an addition to an alkali extraction stage. Some delignification is accomplished with oxygen, but if too much lignin has been removed, its antioxidant effect for the structural carbohydrates is lost and oxygen depolymerization of cellulose occurs. The use of oxygen gas leads to cleaner, more uniform-appearing paper. With chemical pulps, oxygen gas has been observed to aid in the breakup and preliminary bleaching of dark fiber bundles or shives, which still contain considerable lignin. A similar action is useful in the cleaning and bleaching of recycled fibers [23,24].

Ozone is an effective color-stripping agent. Because ozone is such a strong oxidant, it is also an effective delignifying agent. If the furnish contains too high an amount of mechanical pulp, excessive ozone is consumed and significant yield is lost because of delignification. Little brightness is gained during ozone delignification. Some yellowing may even develop. Combinations of bleaching methods that include an ozone stage show promise [17,18]. When oxygen is used for preliminary delignification and pulp cleaning, ozone may be used for color stripping and brightening. A final bleaching is readily accomplished with hydrogen peroxide [17].

TRENDS AND CURRENT RESEARCH

Several avenues are often explored to solve a problem. What effect results in one area will have on another area is often unknown. This is especially true in the area of paper recycling.

The trend in the nature of the agents used for bleaching recycled pulps is clearly toward the elimination of chlorine and chlorine compounds. Because chlorine compounds are especially useful in color stripping and delignification, replacement reagents are likely to be FAS, ozone, and oxygen, which may be used in combination with hydrogen peroxide or dithionite. Peracetic acid is being investigated on a laboratory scale [18]. Because chlorine and hypochlorite are such effective and inexpensive bleaching agents, there are attempts to overcome the environmental disadvantages by other means, such as adjustment of processing conditions or recycle and recovery of chlorinated effluents.

Attempts are continually being made to improve sorting systems for recycled fiber. The better the control of the incoming paperstock, the better the bleach system can be tailored. Bleaching research has been conducted on unsorted municipal wastes and on various synthetic mixtures to simulate the results from different sorting systems [17]. The implication for recycled fiber bleaching is the ease with which the various fiber mixes can be bleached to the desired brightness and color specifications.

The proportion of mechanical pulp fiber in any recycled paper mix will increase for two reasons. First, the amount of pure recycled chemical pulp paper is very limited; at least for the near future, anticipated recycle stock mixes will contain increasing amounts of mechanical pulp [17]. Second, the long-time trend to replace chemical pulps in many paper products with a higher proportion of less expensive mechanical pulp fiber promises to continue. If the extensive research on high yield pulp color reversion reaches a successful conclusion, mechanical pulps will penetrate the market even further.

For many years, the goal of research on inks and dyes has been to improve binding and permanence. Now, the widespread recognition of the need to increase recycling may change the development philosophies of paper dye and ink suppliers. New materials are needed that will have good adhesion in service yet be amenable to rapid and simple removal techniques.

The rapidly emerging field of biotechnology includes applications to virgin pulp bleaching and to recycled fiber bleaching [25]. One technique that assists the bleaching of chemical pulps is to treat the unbleached pulp with hemicellulases and thereby solubilize a portion of the hemicellulose to which residual lignin is attached. Enzymes would also be expected to be effective in removing organic contaminants such as grease or oils from secondary fiber.

Another consideration is acceptance of lower paper brightness. For many purposes, paper brightness demands may be unnecessarily high. However, these demands are mar-
kct and competition driven. There is some evidence that consumers may be willing to accept lower brightness if they know that the product contains a high proportion of recycled fiber. Nevertheless, success in producing high brightness products from 100 percent recycled fiber could help maintain the market demand for higher brightness consistent with economics and good environmental practice.

REFERENCES

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