Kirk-Othmer Encyclopedia of Chemical Technology.

PULP BLEACHING

1. Introduction

Pulp fibers currently produced from the pulp and paper industry can be classified into three different kinds: chemical pulps, mechanical pulps, and deinked (recycled) pulps. The principle objective of bleaching any type of pulp is usually to increase the pulp brightness, which is defined as reflectance measured at a wavelength of 457 nm. This article is based on the 4th edition article, however, now the emphasis is placed on more environmentally friendly bleaching processes and recent new developments.

2. Chemical Pulp Bleaching

2.1. Introduction

Chemical pulp is produced by cooking the wood or non-wood fibrous raw materials in an aqueous solution of chemicals that breaks down and dissolves lignin, and allows the fibers to separate. The dominant kraft process uses an alkaline sulfide solution and produces pulp that is both stronger and darker in color than sulfite pulps made with acidic liquor. It is impossible to remove all of the lignin from the fibrous raw material during pulping no matter what processes are used. The residual lignin content in chemical pulp accounts for 2–5% of the mass, and is responsible for the dark color of the unbleached pulp. Pulp bleaching is usually the next unit operation to remove the residual lignin almost totally in the production of fully bleached chemical pulps. Commercially, a chemical pulp bleach plant is a multistage process, usually with washing between stages to limit chemical consumption. A shorthand notation is used to describe a bleaching sequence. A single capital letter is designated to an individual bleaching agent or chemical treatment used in each bleaching stage of the sequence. In accordance with the Paptac Bleaching Protocol, they are

- Chlorination (C)Reaction with elemental chlorine in acidic medium
- Alkaline Extraction (E)Dissolution of reaction products with NaOH
- Chlorine Dioxide (D)Reaction with ClO_2 in acidic medium
- Oxygen (O)Reaction with molecular oxygen under pressure in alkaline medium
- Hypochlorite (H)Reaction with hypochlorite in alkaline medium
- Peroxide (P)Reaction with peroxide in alkaline medium
- Ozone (Z)Reaction with ozone in acidic medium
- Enzymes (X)Catalyze xylan hydrolysis and aid in lignin removal using xylanase

2.2. Elemental Chlorine-Free Processes

Elemental chlorine was the main delignifying agent in a bleach plant before 1980. At that time, the typical bleaching sequence would be C_dE_oDED (C_d = chlorine with a small amount of chlorine dioxide added; E_o = alkaline reaction with oxygen; D = chlorine dioxide; E = alkaline extraction). In a chlorination stage, some of the applied chlorine ends up as covalently bound chlorine in the lignin structure, either before or after dissolution of the lignin. On average, 6 kg of organically bound chlorine is discharged per tonne of conventional softwood kraft pulp bleached by a C_dE_o prebleaching sequence. Most of the chlorinated organic compounds are toxic and some are bio-accumulative. The discovery of these compounds has raised public concern on the use of elemental chlorine in pulp and paper manufacturing processes.

Because of the environmental impact associated with the use of elemental chlorine in the bleach plant, the so-called elemental chlorine-free (ECF) bleaching processes emerged. In these processes, the main chemical is chlorine dioxide. Chlorine dioxide has different chemical properties from elemental chlorine. Recently, studies have found that all chlorine-related compounds produced during chlorine dioxide bleaching are biodegradable and do not persist in the environment (1). In modern mills using ECF bleaching, no correlation between discharges of organochlorine ($<$ 1.5 kg/ton of pulp) and toxicity is found. Typical ECF processes include the $ODE_{op}DED$ sequence (O = oxygen; E_{op} = alkaline extraction with oxygen and hydrogen peroxide).

The ECF bleaching technology is one of the methods that could be used to achieve lower organochlorine emissions as measured by AOX (Adsorbable Organic Halides) proposed by the Oslo and Paris Marine Commissions (OSPARCOM).

2.3. Totally Chlorine-Free Processes

In contrast to the ECF technology, the totally chlorine-free (TCF) bleaching processes do not use chlorine dioxide or any other chlorine containing chemicals. In TCF process, only oxygen-based chemicals, such as molecule oxygen, hydrogen peroxide, ozone, and peroxy acids are used. The TCF technology is often used in combination with extended delignification in the pulping process.

A pretreatment stage, such as a chelation stage for metal management (Q), followed by an alkaline peroxide stage (P) was the key for the first commercial TCF chemical pulp bleaching sequence (1). Many of the TCF sequences are variations of a QP sequence. The brightness obtained depends on the incoming kappa number and the effectiveness of metals management. Multiple peroxide stages can be complemented by running at very high temperature (1). For sulfite pulps, the brightness can approach 90% ISO for hydrogen peroxide charges of $<$ 3–4%.

Hydrogen peroxide is the primary chemical in any TCF sequences. It has been shown that brightness and brightness stability are optimum when hydrogen peroxide is applied at the end of a sequence that includes an ozone stage. Sequences such as OZP, OZEP, $OZE_{op}P$, and $O(QZ)QP_o$ [P_o = peroxide with oxygen] can be used to produce acceptable market-grade softwood pulps (2). A peroxy acid stage, ie, peracetic acid, Pa; or Caro's acid, Px, can function as an activation stage in a TCF sequence. Examples are $OZE_{op}PaP$ and $OQE_{op}PaP$.

2.4. Bleaching Agents

Presently, all important chemical pulp bleaching agents are oxidants with the exception of caustic soda.

2.4.1. Oxygen

In a bleach plant, oxygen can be used in both the delignification stage (the so-called oxygen bleaching or delignification) and E_{op} or E_o stage. The oxygen delignification or prebleaching was commercialized during the late 1960s and the early 1970s in Sweden and South Africa. Since then, it has grown remarkably as a result of continuing efforts by the industry to improve effluent quality. Because the effluent from the oxygen delignification stage contains no chloride ion or chlorine compounds it could be fully recycled into the cooking waste liquor recovery system. The technology is now becoming the standard of the industry. In addition, the E_o technology, uses oxygen to enhance the effectiveness of the first caustic extraction stage, has become universal.

The oxygen delignification process is commercially operated at either high (23–27%) or medium (10–12%) pulp consistency. Nearly all of the early installations were designed for high consistency operation. However, the recent installations are usually medium consistency systems. Thanks to the development of the high-shear mixer, oxygen is dispersed in the pulp as fine bubbles. The medium consistency systems have a capital cost advantage over the high consistency ones because expensive dewatering equipment is no longer needed. A single oxygen delignification stage is commonly limited to 40–50% delignification degree to prevent pulp strength loss, due to relatively low selectivity of oxygen in the delignification process. The addition of a magnesium salt as a cellulose protector helps in this regard. Oxidized kraft pulping liquor can be used as a source of the alkali to promote the reaction. Typical conditions for the oxygen delignification stage are 2.5% NaOH, 30 min, 500 kPa (5 atm), 110°C at 27% consistency, and 3% NaOH, 60 min, 500 kPa, 90°C at 12% consistency. Oxygen consumption is typically 2–3 %.

More recently, the two-stage oxygen delignification technology (ie, Oxytrac process) has been developed. Here, the delignification degree can reach about 60% without causing a significant decrease in pulp strength (3).

When oxygen is added to the first caustic extraction stage, it is known as the E_o technology. An absolute oxygen pressure of 250 kPa, maintained for 3 min, is sufficient. Addition of 5- kg oxygen per ton of pulp in the E_o stage could reduce chlorine dioxide charge in a following stage by 5 kg (4).

2.4.2. Chlorine Dioxide

Chlorine dioxide is the most important chemical used for bleaching chemical pulp in a modern bleach plant. The environmental impact of using chlorine dioxide to bleach chemical pulps is deemed to be significantly less than that of elemental chlorine.

Chlorine dioxide is a strong oxidizing agent, when present in sufficiently high concentration, it becomes explosive. A variety of processes are available for safe on-site generation. All involve reaction of a reducing agent with sodium chlorate ($NaClO_3$) in acid medium. The main differences among these processes are the amount of chlorine in the ClO_2 solution, sodium sulfate (Na_2SO_4), and acid by-products. The reducing agent can be sulfur dioxide (SO_2), methanol (CH_3OH) or hydrogen peroxide (H_2O_2).

Chlorine dioxide is used in both the delignification and the brightening stages. It reacts with free phenolic groups, aliphatic double bonds, resulting in demethylation and ring cleavages. However, chlorine dioxide, unlike chlorine, is relatively unreactive towards fully etherified phenolic units in lignin. It is nearly inert toward cellulose and other carbohydrates in the pulp.

Chlorine dioxide brightening stages are conducted for 2–5 h at 10–12% consistency, 60–80°C and pH 3–5. The chemical charge varies from 0.1–1.2% depending on the type of pulp, the length of the sequence and the number of chlorine dioxide stages present.

2.4.3. Sodium Hydroxide

Sodium hydroxide is used in the extraction stage (E), oxygen delignification stage (O) and peroxide stage (P).

The purpose of the alkaline extraction stage following a D stage is to further solubilize the reacted lignin. Typical conditions are 1–2 h at 60–90°C and 10–12% consistency. Oxygen is very frequently added (E_o), either alone or with hydrogen peroxide (E_{op}) to enhance the lignin removal and to decrease downstream bleaching chemical costs.

2.4.4. Hydrogen Peroxide

The growth in the use of hydrogen peroxide in chemical pulp bleaching since the late 1980s is attributed to environmental constraints, and improvement in economics and pulp quality. Hydrogen peroxide has a variety of applications in chemical pulp bleaching. These include final brightening, addition to caustic extraction stages alone or with oxygen (E_p and E_{op}), and in a predelignification stage at the beginning of the sequence. Typical tower conditions are 1–2 h, 80°C, pH 11 and 10% consistency. Addition of peroxide with oxygen to a first caustic extraction stage allows a significant decrease in the amount of chlorine used in the preceding stage. Addition to a second caustic extraction stage (E_2) could reduce the chlorine dioxide charge in the D_1 or D_2 stage.

2.4.5. Ozone

The ozone bleaching technology has been the subject of laboratory and pilot plant studies for many years but it remained uncommercialized until the 1990s. Because ozone is such a powerful oxidizing agent it tends to react with the pulp indiscriminately. Therefore, its application must be carefully controlled to prevent pulp strength loss.

In an ozone stage (Z) the main process variables that influence the ozone-pulp reactions, pulp properties, and commercial viability, are pulp consistency, ozone charge, pH, time, temperature, chemical additives, transition metal ions, and carryover. The commercial ozone delignification technology is performed either in medium consistency (8–12% pulp consistency) or high consistency (25–35% pulp consistency), at pH range of 2–3 and 40–70°C. The ozone charge is usually limited to 1%, and mostly $< 0.5\%$ since a higher ozone charge will have a more pronounced negative effect on the pulp strength.

One of the benefits of using an ozone stage in a bleaching sequence compared to chlorine and chlorine dioxide stage is that its filtrate could be recycled to existing chemical recovery processes.

Ozone can also be used in substituting chlorine dioxide in the D_o stage of a $D_oE_{op}DED$ sequence, which was denoted as a (DZ) stage, chlorine dioxide treatment first, followed by ozone treatment, or (ZD) stage, ozone treatment first, followed by chlorine dioxide treatment. It was reported (5) that the combination of chlorine dioxide and ozone are effective to decrease both the chemical cost and AOX formation in an ECF sequence of kraft pulps. The delignification efficiency depends on the order of addition of the two chemicals. On a conventional kraft pulp without oxygen delignification (DZ) is superior to (ZD), for an oxygen delignified pulp (ZD) is slightly better than (DZ).

2.4.6. Peroxy Acids

A peroxy acid, or peracid, is an acid that contains a perhydroxyl group (—OOH). The common ones are peracetic acid and the Caro's acid (mono peroxy sulfuric acid). They are powerful oxidizing agents. Caro's acid, H_2SO_5, is a dibasic acid in which the protons are attached to the oxygen of the hydroxyl group and the perhydroxyl group. The Caro's acid anion, HSO_5^-, is a considerably weaker acid than HSO_4^-, the anion of sulfuric acid.

In pulp bleaching, peracetic acid can function as a delignifying or a brightening agent. Typically, the delignification conditions for peracetic acid are initial pH 6–7, temperature 70–80°C, and reaction time 60–180 min at medium consistency. The peroxy acetic acid consumption is 3-kg/delignified kappa unit. As a brightening agent, peracetic acid improves brightness, brightness reversion, and other optical properties of the bleached pulp. As a postbrightening agent, peracetic acid can be applied in the high density storage tank for the production of wood-free paper at integrated pulp and paper mills, or at paper mills using market pulp. At near neutral pH levels, the brightening effect of peracetic acid is very rapid. Most of the improvement in optical properties occurs during the first few minutes, even at low temperatures and consistencies. In this application, 1–2-kg peracetic acid per tonne of pulp is sufficient to increase ISO brightness by 1.5–2.5 units.

Also, it is found that the residual peracetic acid efficiently prevents microbial growth in paper machines.

Furthermore, peracetic acid can limit brightness reversion of the bleached pulp and inhibits brightness reversion during beating. It is also shown to be effective in bleaching pigments and fillers (6).

It should be noted that peracetic acid and Caro's acid have similar effects as delignifying and bleaching agents. Neither has common usage in the industry.

2.4.7. Chlorine

Chlorine has been largely phased out as a delignification chemical in North America. However, in Asia and other parts of the world, chlorination is still commonly practised. The mechanisms by which delignification occurs include demethylation, alkyl-aryl ether cleavage, aromatic substitution, and oxidation. The important process variable is pH, which is usually at ~ 2. Modern chlorination stages are run at either low pulp consistency (3–4% consistency) or medium (10–12% consistency) and a temperature of 40–60°C. A retention time of 30–60 min is commonly used. Chlorine is usually applied at a charge proportional to the lignin content which is measured as "kappa number" of the pulp entering the stage. The chlorine charges can vary widely depending on whether softwood or hardwood is the raw material, whether a preceding oxygen stage is used, and whether new extended delignification technology is used in the pulping step. Chlorine charges of 3–7% is quite common.

The generation of chlorinated organics is inevitable during chlorination. These chlorinated compounds have a negative effect on the environment. These organics include chloroform, and dioxin. They are considered to be very harmful to the environment and are deemed to be carcinogenic.

2.4.8. Hypochlorite

Calcium hypochlorite, $Ca(OCl)_2$, was among the earliest chemicals to be used for pulp bleaching. Both calcium and sodium hypochlorite are cheap and capable of bleaching the pulp to high brightness. Presently, the consumption of hypochlorite is decreasing because of the chloroform ($CHCl_3$) generation, which is strictly regulated by government agencies in North America. Hypochlorite stage (H) is generally applied after chlorination and caustic extraction, eg, in sequences such as CEHDED, CEHD, CEHEH, and CEHP. Aside from the generation of chloroform, its chief drawback is its tendency to degrade cellulose, especially when the pH falls < 8. The typical conditions for the hypochlorite stage (H) are 1–4 h at 10–12% consistency, 30–40°C and initial pH of 11. Shorter time and higher temperature may be used. Chemical charge is normally in the range of 0.5–1.5% as available chlorine.

2.4.9. Enzymes

Two different strategies have been developed in using enzymes for chemical pulp bleaching; (1) hemicellulases (particularly xylanases) as a pretreatment for enhancing the chemical removal of lignin in multistage bleaching sequences, (2) ligninases or laccases for direct delignification. The first one has led to a successful commercial mill-scale process, while the latter is still in the exploratory stage and awaits possible commercialization.

The benefit in using enzyme for pulp bleaching depends on the bleach sequence used, the residual lignin content of the pulp, the final target brightness and environmental concerns of the mill. The main goals have been directed toward reducing the charge of chlorine-containing chemicals in the bleach plant and lowering the AOX content of the bleach effluent. Enzyme has been used in conventional chlorine-containing sequences, such as (C/D)EDED, in ECF sequences and TCF sequences.

2.5. New Developments

2.5.1.

2.5.1.1. Dimethyl dioxirane Delignification. DMD has been demonstrated to be a very selective delignification agent (7). It can be generated on site by reacting Caro's acid with acetone,. The acetone acts essentially as a catalyst and is regenerated during the oxidation of the pulp with DMD. Elucidation of the pulp reaction mechanisms remains a subject of research activity (8). The commercialization of this technology remains to be seen.

2.5.1.2. Hydrogen Peroxide Activators. Nitrilamine (cyanamide) can be added to a hydrogen peroxide stage (9) to increase the brightness threshold by 2–3 points. This effect will allow the mill either to lower peroxide charges or to attain higher brightness pulps. The charged nitrilamine would be consumed in the bleaching reaction and converted to urea.

The use of tungstate and molybdate catalysts to activate acidic hydrogen peroxide for delignification reactions has also been investigated (10). Similarly, transition metal-substituted polyoxometalate cluster ions have been proposed primarily for use as delignifying agents (11). Polyoxometalate cluster ions are inorganic analogs of the organic platforms known to control the activity of transition metals in enzymes that selectively catalyze the oxidation of lignin. The polyoxometalate cluster can be reoxidized after reaction with lignin, for recycle and reuse. Air and hydrogen peroxide have been used to reoxidize the catalyst. It has been shown that application of a silicon-tungsten-manganese-based cluster ion to an oxygen-delignified softwood kraft pulp at 125°C for 2 h decreases the kappa number from 35 to 5, and only reduces the viscosity slightly (from 34 to 27 cP). Most of the work on this topic is still at the development stage.

3. Mechanical Pulp Bleaching

3.1. Introduction

Unlike chemical pulps, the separation of wood fibers during mechanical pulping processes is achieved mainly by mechanical means, such as grinding and refining. As a result, these pulps are collectively called mechanical pulps and they include Stone Groundwood Pulp (SGW), Thermo-mechanical Pulp (TMP), Chemi-thermo-mechanical Pulp (CTMP), and Alkaline Peroxide Mechanical Pulp (APMP). The world total design capacity for mechanical pulps is about 38.2 million ton/year.

Like chemical pulps, lignin again is the main contributor to the color of mechanical pulps. The brightness increase for mechanical pulps and other high-yield pulp is achieved by modifying the lignin structures (chromophores) in the pulp furnish. The process sometimes is referred to as brightening to distinguish it from lignin-removing bleaching methods for chemical pulps. Commercial brightening agents are hydrogen peroxide and sodium hydrosulfite (sodium dithionite).

3.2. Process Description

3.2.1. Chelation (the Q stage)

Transition-metal ions, such as manganese, iron, and copper, can induce peroxide decomposition under the typical peroxide brightening conditions, thus, decreasing the process efficiency and increasing the cost. Therefore, it is important that transition-metal ions are removed from pulp fibers prior to a peroxide stage.

Organic compounds containing both amines and carboxylic acids in the structures, such as DTPA (diethylenetriaminepentaacetic acid) and EDTA (ethylenediaminetetraacetic acid), are the main chemicals used to remove transition-metal ions from mechanical pulp in a pretreatment stage, called the chelation stage (Q). Either DTPA or EDTA can form highly stable complexes with transition-metal ions. Typically, the penta sodium salt of DTPA is used. The chemical is usually mixed thoroughly with the stock before a hydrogen peroxide stage (P). A convenient procedure for this is to add the chelant to the low consistency stock in the cleaning system, or when the stock is delivered to the decker/press. The chelated metals are then removed in the dewatering stage via a press or decker. The total transition-metal ion concentration in the treated pulp would be significantly reduced.

3.2.2. Peroxide Brightening/Bleaching

The peroxide bleaching chemistry for chemical and mechanical pulps is very different. For the chemical pulp, the goal is to maximize the removal of lignin while for mechanical pulp the objective is to brighten the pulp with almost no dissolution of wood constituents, thus preserving pulp yield. The brightening of (chemi)mechanical pulps is achieved by selectively eliminating chromophores. During bleaching, perhydroxyl anion (OOH^-), which is a strong nucleophile, converts the electron-rich chromophores typified by α, β-unsaturated aldehydes and ketone, and phenolic ring-conjugated ethylenic or carbonyl groups to their non-chromophoric counterparts.

The peroxide bleaching is usually carried out by mixing the pulp fibers with the bleach liquor containing hydrogen peroxide, caustic soda, sodium silicate (41°Be), water and sometimes epsom salts. The resulting mixture is then sent to a bleaching tower for 1–5 h, at 50–80°C. At the completion of the required time, some acids, typically SO_2 water, are used to lower the pH to 4.0–6.5. In a modern mill, a press, such as a twin-roll press, is used to increase the pulp to a consistency of 25–35%, which allows the removal of much of the undesired material, such as anionic trashes, from the pulp.

Several factors influence the performance of a peroxide stage, including consistency, retention time, and temperature. If the pulp consistency is >18%, the process is usually referred to as high consistency (HC) technology while the medium consistency (MC) process is usually operated at 10–12% pulp consistency.

3.2.3. Hydrosulfite Bleaching

Hydrosulfite, sometimes also referred to as dithionite ($S_2O_4^{2-}$), is a strong reducing agent. In the mill, usually sodium hydrosulfite is used (although zinc hydrosulfite was also used earlier). Hydrosulfite bleaching (Y) is preferred over peroxide bleaching if only modest brightness gains [eg, 4–8 International Standard Organization (ISO) units] are required.

Hydrosulfite selectively converts the chromophores into colorless or less colored structures, with almost no dissolution of pulp components, thus is a lignin-preserving bleaching chemical. The reactive species in a Y stage is believed to be a sulfur dioxide radical ion (SO_2^{2-}), which is formed through homolytic splitting of the weak sulfur to sulfur bond in hydrosulfite. The sulfur dioxide radical ions will then attack the chromophoric systems and convert them to the structures that are essentially colorless. The commercial hydrosulfite, whether in powder or solution form, often contains bisulfite, which also contributes to the discoloration of chromophores.

An important consideration in a Y stage is to exclude air/oxygen from the system as much as possible, to avoid loss of bleaching power. The hydrosulfite bleaching can be performed in a refiner, a stock chest, or a specially designed tower. The temperature is usually in the range of 50–70°C, the pH $\sim$ 6, and the bleaching time $\sim$ 60 min although the brightness development. is extremely rapid.

3.2.4. Multiple Bleaching Stages

If a large brightness gain (>15 ISO units) is required, a two bleaching stage sequence can be used. The PP (two peroxide stages are arranged in a sequence) and PY (a peroxide stage, followed by a hydrosulfite stage) processes are often practised commercially for this purpose.

3.3. New Developments

3.3.1.

3.3.1.1. The Q_y Process. Recently, it was reported that the addition of a small amount of sodium hydrosulfite to the DTPA chelation stage (Q) improves the removal of transition-metal ions from a TMP furnish, and consequently, the performance of the subsequent peroxide stage (12). The process is denoted as the Q_y process, the so-called sodium hydrosulfite assisted chelation. Mill trials were conducted in an Eastern Canadian mill. The results of these trials confirmed the laboratory results and the process was fully incorporated into the mill's peroxide bleaching system. Since it became fully operational in August 1997, the production of 70% ISO paper has decreased the bleaching chemical cost by 25%.

3.3.1.2. The P_M *Process (13).* In this process, sodium silicate and part (or all) of the sodium hydroxide are mixed with pulp first. After 30 s to 1 min, the required amount of hydrogen peroxide (and the remaining sodium hydroxide if needed) is then added to the pulp. This sequential addition of chemicals, in the above specified manner, decreases the peroxide decomposition, thus increasing the bleaching performance.

It is highly preferable that the P_M process is preceded by the Q_y process (12). The Q_y process removes a significant portion of the transition-metal ions present in the pulp. In the Q_y process, a chelating agent, such as DTPA, is added to the unbleached pulp, along with sodium hydrosulfite. After the addition of the chelant and the reducing agent, the pulp slurry is dewatered in a press to remove the chelated transition-metal ions; it is transferred into a slurry tank and then into the bleach process.

3.3.1.3. Using Weak Alkali Source to Bleach Mechanical Pulps. Traditionally, sodium hydroxide is the alkali source for the peroxide bleaching of mechanical pulps. Recently, there have been some studies examining the effect of using weak alkali sources such as sodium carbonate (14, 15), magnesium oxide (MgO) and/or magnesium hydroxide ($Mg(OH)_2$) (16), and magnesium carbonate (17) on peroxide bleaching. These weaker alkali sources produced a bleached pulp with slightly lower brightness (1–2 ISO units) than the NaOH based process under otherwise identical conditions. However, the anionic trashes and COD, on the other hand, were found to be significantly lower. The bulk (specific volume) of the bleached pulps were higher in comparison with the conventional process.

4. Bleaching of Recycled Pulps (Secondary Fibers)

4.1. Introduction

The need to utilize recycled fibers has increased in recent years, due to rapid decrease of the landfill sites, market pressures resulting from public awareness of issues like sustainable development, government legislation, and a dwindling supply of virgin fibers in North America. As a result, recycled fibers are increasingly being considered to be important alternative fiber sources.

The quality and brightness of the recycled fiber furnish will dictate its end use. The removal of colored complexes, such as dyes and other unwanted materials (ie, ink and stickies) is an important operation to produce a recycled pulp with good properties, including good optical properties. Chlorine–based chemicals, such as hypochlorite, were used to bleached recycled fibers. However, growing public concerns about the negative environmental impact of chlorinated organic compounds generated in these processes have led to the adoption of more environmentally friendly processes in the mill. Totally chlorine free (TCF) processes employing non-chlorine containing chemicals are some of the technologies. The common TCF bleaching chemicals for recycled fibers are oxygen (O), ozone (Z) and hydrogen peroxide (P), which are oxidative chemicals, and sodium hydrosulfite (Y) and formamidine sulfinic acid, FAS (F), which are reductive chemicals (18).

4.2. Bleaching Agents

4.2.1. Hydrogen Peroxide

Hydrogen peroxide is very effective in bleaching recycled pulp. The conditions are similar to those used in the bleaching/brightening of mechanical pulps. It can be performed in a pulper, or a bleaching tower, or a disperser. The bleaching liquor usually contains hydrogen peroxide, caustic soda, DTPA and/or sodium silicate, and/or other peroxide stabilizers. If it is applied to the pulper, a soap or surfactant may be added to aid in ink removal.

In most cases, for the same hydrogen peroxide charge, the brightness of the resulting recycled pulps is usually lower than the bleached mechanical pulp. This is due to the fact that the recycled furnish contains some residual ink particles.

Peroxide bleaching of recycled pulp could take place in a disk-type disperser, the time is very short, however, the temperature is high (90–95°C) and the pulp consistency is also very high (30–35%). This method effectively minimizes the brightness loss due to break-up of the ink particles, and improves the efficiency of the subsequent flotation operation.

4.2.2. Ozone

Ozone is an excellent bleaching chemical for recycled pulps containing minimal amount of mechanical pulp fibers. Ozone is particularly reactive toward dyes. The mechanical properties of the furnish, such as tensile and burst, could be improved by the ozone treatment.

4.2.3. Formamedine Sulfinic Acid

Formamidine sulfinic acid, $CH_4N_2O_2S$, sometimes also called thioureadioxide, can be used either alone or in sequence to bleach recycled pulps. FAS is a strong reducing agent and is thus effective in removing dyes. In such application, FAS is more effective than sodium hydrosulfite. The optimum process conditions for FAS treatment are initial pH of $\sim$ 10 (with the addition of caustic soda), 60–90°C, 30–60 min.

FAS is normally delivered to the mill in the form of powder. Its solubility is 30 g/L at 20°C. FAS is relatively stable at room temperature. It can decompose when exposed to moist air. When heated to $\sim$ 120°C it rapidly degrades in exothermic reaction and evolves into sulfur dioxide gas.

4.2.4. Hydrosulfite

Sodium hydrosulfite is also very effective in bleaching recycled pulp (secondary fibers) because sodium hydrosulfite is a strong reducing agent and can effectively react with the dyes in the pulp. Also, most recycled furnish usually contains some mechanical pulps that can be bleached by sodium hydrosulfite.

The bleaching conditions for recycled pulp by sodium hydrosulfite are very similar to those for mechanical pulps. If the furnish, such as (mixed office waste) MOW, contains mainly chemical pulps, significant brightness gain could be achieved by performing a hydrosulfite (Y) stage at a much higher temperature, 80–100°C and at pH of 7.0.

4.3. New Developments

4.3.1.

4.3.1.1. The Direct Borohydride Injection (DBI) Process (19). This is a reductive bleaching/color stripping process for recycled pulps. The process involves the sequential addition of bisulfite solution and sodium borohydride solution to the recycled pulp in medium to high consistency in sequence via an appropriate mixing equipment. The first chemical, sodium bisulfite solution is commonly available in 38% solution. The second chemical, Borol solution, is a 12% sodium borohydride. A retention time of 3–5 min for the bisulfite before the addition of borohydride is sufficient. Because the quantity of borohydride injected into the pulp stream is so small and also the chemical reaction is so fast, a fast and thorough mixing is important to produce the expected results. The best mixing conditions are found in systems containing a disperser or a MC (medium consistency) mixer, or both. A high temperature, 90°C, or even 110–115°C, is desirable.

4.3.1.2. Using Sodium Silicate and Chelant in the FAS Stage. The most important parameter for an effective FAS stage is the pH. Usually, it starts with an initial pH of $\sim$ 10 and ends at a neutral pH (20).

Sodium hydroxide is the common alkali source for initial pH adjustment. A ratio of FAS to NaOH of 2:1 was demonstrated to be effective (21). It was reported (22) that when sodium silicate instead of sodium hydroxide was used for pH control during the FAS treatment, a better bleaching result could be obtained. This is probably due to sodium silicate, which stabilizes the transition metal ions present in the system and reduces the FAS decomposition. Furthermore, when both chelant and sodium silicate are added to the FAS stage, followed by a peroxide stage (a FP sequence), the final brightness of the resulting pulp is higher than the control. The improved bleaching in the peroxide stage is the result of enhanced removal of transition-metal ions by the combined actions of reduction and chelation in the FAS stage (F).

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