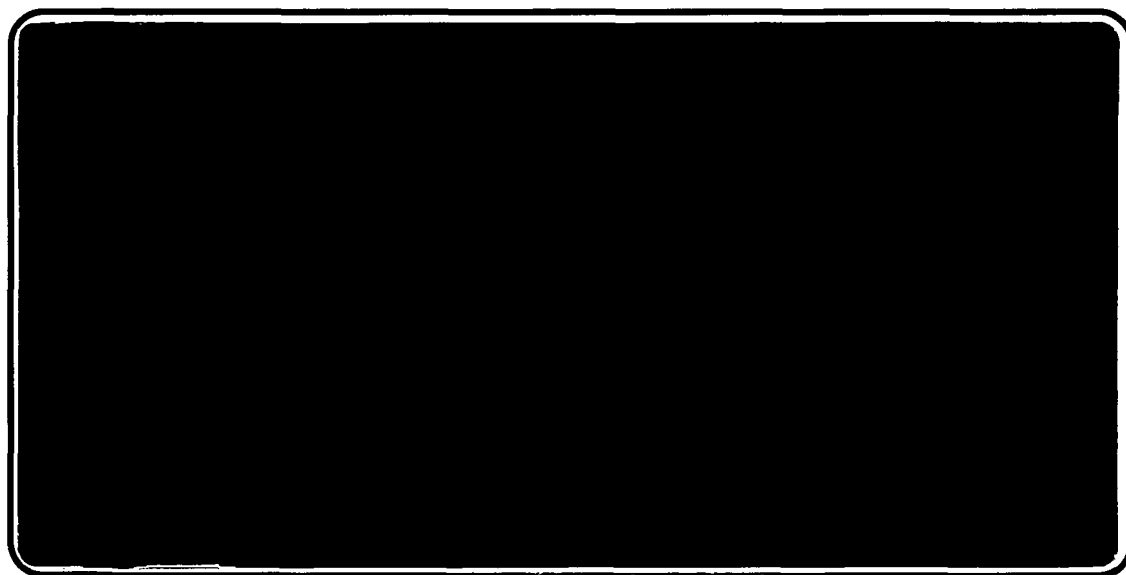




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BLEACHING AGENTS - PULP AND PAPER INDUSTRY

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BLEACHING AGENTS - PULP AND PAPER INDUSTRY

An Article for the Fourth Edition of
The Kirk-Othmer Encyclopedia of Chemical Technology

by T.J. McDonough

The Institute of Paper Science and Technology

Worldwide, more than 50 million tons of pulp is bleached annually, making the pulp and paper industry one of the largest consumers of bleaching chemicals. Most of the pulp bleached is made by separating wood into its component fibers, either chemically or mechanically. Mechanical pulp is made either by forcing wood chips through a narrow gap between rotating disks in so-called refiners or by stone grinding of logs. Its chemical composition closely parallels that of the original wood, the major components being cellulose, other polysaccharides ("hemicelluloses"), lignin, and minor amounts of solvent extractable materials. Chemical pulp is made by cooking the wood in an aqueous solution of chemicals that are able to break down and dissolve lignin, allowing the fibers to separate. The dominant kraft, or sulfate, process uses an alkaline solution and produces pulp that is both stronger and darker-colored than sulfite pulps made with acidic liquor. A third broad class is made up of pulping processes that rely on various combinations of chemical and mechanical methods. Semichemical and chemimechanical pulps, for example, are made by disk refining of chips after a mild chemical treatment.

The major objective in bleaching all types of pulp is usually to increase the whiteness of the pulp, as measured by its "brightness," which is defined as reflectance measured at a wavelength of 457 nm. Depending on end use, however, other criteria may rival brightness in importance. These include cleanliness, or freedom from particles of bark and unpulped wood particles; resistance to yellowing upon irradiation or storage; and removal of hemicellulose and extractives.

CHEMICAL PULP

Virtually all of the color of any pulp resides in its lignin component. It is not possible to remove all of the lignin from the wood during pulping because concurrent cellulose damage would seriously weaken the fibers. Pulping is therefore terminated when 5-8% of the original lignin remains. Bleaching may therefore be regarded as a more selective continuation of the pulping process, but there are important distinctions to be made between these two phases of delignification. Side reactions during pulping cause the residual lignin to be both darker in color and more tightly bound to the fiber than native lignin. From a practical point of view, a more important distinction concerns the fate of the organic material removed. Spent pulping liquors are recycled to a chemical recovery system, where they are concentrated and burned to generate energy. Bleaching effluent, on the other hand, is typically contaminated with chloride ion and chlorine compounds, making it difficult or impossible to recycle it to the recovery system. It is therefore necessary to treat and discharge the bleaching effluent. Associated environmental concerns are presently causing rapid changes in bleaching technology.

Bleaching Sequences. The application of increasing amounts of any bleaching chemical results in progressively smaller brightness increases per unit weight of chemical added. Because the asymptotic limit is usually far below the final brightness target and because it is approached only at high chemical charges, single-stage bleaching is both ineffective and uneconomical. As a result, chemical pulps are invariably bleached in multistage processes, usually with washing between stages to limit chemical consumption. A shorthand notation for bleaching sequences uses single capital letters to designate individual bleaching agents as follows: C=chlorine, E=caustic extraction, D=chlorine dioxide, O=oxygen, P=hydrogen peroxide, H=hypochlorite, Z=ozone. Stages employing only one chemical are designated by a single letter; those using combinations are designated by a variety of notations, such as C_D, D/C, (C+D), (CD), etc. Sequences of from three to six stages are common. The first two or three usually remove the bulk of the residual lignin with little or no brightness increase and comprise the delignifying partial sequence. Examples are CE, (CD)E, O(CD)E. The final one to four stages accomplish a large brightness increase with little lignin removal and comprise the brightening partial sequence. Examples are D, DP, DED, and D(EP)D.

Desirable Attributes of Bleaching Agents. An ideal bleaching agent for chemical pulp would have high selectivity, reactivity, efficiency, and particle bleaching ability, while simultaneously having low equivalent weight

and low potential for harm to the environment. With the exception of caustic, all important chemical pulp bleaching agents are oxidants. Low equivalent weight is desirable because it translates to a small chemical requirement for the transfer of a given number of electrons. Efficiency refers to the degree to which these electrons are transferred in productive processes, such as lignin depolymerization and chromophore destruction, as opposed to unproductive ones, such as decomposition and soluble product fragmentation.

Chlorine. Chlorine is used either in the first stage of the sequence or in the stage immediately following an oxygen predelignification stage. Its chief function is to render most of the residual lignin soluble in alkali, and it is always followed by a caustic extraction stage. The mechanisms by which solubilization occurs include demethylation, alkyl-aryl ether cleavage, aromatic substitution, and oxidation. An important variable is pH, which is kept below 2 to avoid excessive hydrolysis of chlorine to hypochlorous acid, which can attack cellulose. A salient feature of chlorination is its extreme rapidity. In a perfectly mixed system, the bulk of the reaction is complete within seconds, and a subsequent slower phase is virtually complete within a few additional minutes. This, together with the extreme slowness of diffusion of chlorine in pulp suspensions, makes good mixing very important. Accordingly, traditional chlorination stages were conducted at low pulp consistency (3-4% dry fiber on pulp suspension weight basis) to facilitate good mixing and at low temperature (5-30°C) to decrease the rate of reaction relative to that of diffusion and to increase selectivity for lignin. Modern chlorination stages are run at either low or medium (10-12%) consistency and higher temperature (40-60°C). Medium consistency operation has been made possible by the introduction of high-shear, fluidizing mixers. High temperature operation is facilitated by good mixing and also by the selectivity improvement that comes from substituting chlorine dioxide for part of the chlorine used. A retention time of 30-60 minutes is provided to allow for process upsets and less-than-perfect mixing. Chlorine is applied at a rate that is proportional to the lignin content (as measured by "kappa number") of the pulp entering the stage. This 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% have been common, but an environmentally-driven downward trend is evident. This has arisen out of concern over possible environmental effects of chlorinated organic byproducts. The formation of these byproducts is now commonly controlled by substituting chlorine dioxide for part or all of the chlorine used.

A relatively small amount of lignin dissolves during chlorination; most is removed in the subsequent caustic extraction stage. The charge of caustic is proportional to the amount of chlorine in the previous stage and is controlled to maintain an exit pH of 10.5 or above. Typical conditions are 1-2 h at 60-80°C and 10-12% consistency. Oxygen is frequently added, either alone or with hydrogen peroxide, to effect more complete lignin removal and to decrease downstream bleaching chemical costs. Alternatively, the benefit of oxygen addition may be realized in the form of a reduction in chlorine application to meet environmental demands.

Chlorine Dioxide. Chlorine dioxide offers a unique combination of low equivalent weight (13.5 vs. 35.5 for chlorine), extremely high selectivity for lignin, high efficiency, ability to bleach to very high brightness, and good particle bleaching ability. It is versatile, inasmuch as it can be used both to brighten and to delignify, and in the latter role, it interacts synergistically with chlorine. Furthermore, it is less likely than chlorine to have significant environmental impact since it forms a much smaller amount of chlorinated organic byproducts for a given bleaching effect. Although it is toxic and, when present in sufficiently high concentration, explosive, a variety of processes are available for safe on-site generation. All react a reducing agent with sodium chlorate in acid medium; significant differences between them include their relative rates of production of chlorine, saltcake, and acid byproducts, all of which can present disposal problems. The reducing agent is sulfur dioxide, methanol, or chloride ion.

Chlorine dioxide is widely used in chemical pulp bleaching. 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. Reactions occur with free phenolic groups and aliphatic double bonds and encompass demethylation and ring cleavage reactions. However, chlorine dioxide, unlike chlorine, is relatively unreactive toward fully etherified phenolic units in lignin. It is nearly inert toward cellulose and other carbohydrates in the pulp.

An increasingly important role for chlorine dioxide is as a delignifying agent in the first stage. Small amounts (0.05-0.15%) of chlorine dioxide have been added to chlorination stages for many years, the main objective being to prevent cellulose degradation by chlorine. In this application, chlorine dioxide is believed to act as a free radical scavenger. Substitution of chlorine dioxide for large fractions (50-70%) of the chlorine requirement has also been practiced for a long time but, until recently, in relatively few instances. Growing concern over chlorinated byproducts has changed this, and the use of high levels of chlorine dioxide substitution is becoming widespread.

Furthermore, there is a growing demand for pulp bleached without the use of elemental chlorine, particularly from European markets. To meet this demand, some mills operate for part of the time at a substitution level of 100%. At a substitution level of 50%, the combination of chlorine and chlorine dioxide is more effective than either one alone, bleaching chemical cost is comparable to the cost of using pure chlorine, and effluent quality is improved. Increasing the substitution level beyond 50% generally increases total chemical cost, and operation at 100% chlorine dioxide is significantly more expensive than at 50%. The reason for this is that pure chlorine dioxide does not delignify as effectively as pure chlorine or mixtures with chlorine.

Hypochlorite. Calcium hypochlorite was among the earliest chemicals to be used for bleaching pulp. Both calcium and sodium hypochlorite are cheap and capable of bleaching pulp to high brightness. Hypochlorite is still used, but its use is decreasing because the bleaching reaction generates chloroform, a byproduct which is being strictly regulated by government agencies. Hypochlorite is generally applied after chlorination and caustic extraction, for example, in sequences such as CEHDED, CEHD, CEHEH, and CEHP. Aside from chloroform generation, its chief drawback has been its tendency to degrade cellulose, especially if the pH is allowed to fall to values below about 9. Typical conditions are 1-4 h at 10-12% consistency, 30-40°C, and initial pH 11. Shorter times and higher temperatures may be used if the level of chemical application is tightly controlled. Chemical charge is normally in the range 0.5-1.5% as available chlorine. Future use of hypochlorite will be severely limited by restrictions on chloroform release.

Hydrogen Peroxide. Hydrogen peroxide has a variety of applications in chemical pulp bleaching. These include final brightening, addition, alone or with oxygen, to caustic extraction stages, and in a predelignification stage at the beginning of the sequence. Final brightening is the oldest application and can be done in a dedicated bleach tower, in a pulp storage tower, or in the pulp drying process. Addition of 0.5% or less raises final brightness 1-2 percentage points and significantly improves brightness stability. Typical tower conditions are 1-2 h, 80°C, pH 11, and 10% consistency, but milder conditions are used for storage tower bleaching. 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 E stage reduces chlorine dioxide consumption. Peroxide can be used to predelignify pulp, but it usually does not compete well with oxygen in this application because of its higher cost. Peroxide use will increase as efforts to displace chlorine continue.

Oxygen. The use of oxygen to bleach chemical pulps was first practiced on a commercial scale in 1970. Since then it has grown remarkably as a result of continuing efforts by the industry to improve effluent quality. It was first used in a predelignification stage to remove about half of the lignin in the unbleached pulp. The resulting effluent can be recycled, concentrated, and burned in the chemical recovery system because it contains no chloride ion or chlorine compounds. Oxygen predelignification is now becoming widespread, and most new mills and mill expansions include it. In addition, the use of oxygen to enhance the effectiveness of the first caustic extraction stage has become nearly universal.

Predelignification with oxygen is conducted at either high (23-27%) or medium (10-12%) consistency. Nearly all of the early installations were designed for high consistency operation to provide high interfacial area for efficient oxygen transfer and a continuous gas phase to serve as an oxygen reservoir. The development of fluidizing, high-shear mixers has since enabled the development of medium consistency systems. Oxygen is dispersed in the pulp as fine bubbles before it is fed to an upflow tower. These systems have a capital cost advantage over the high consistency ones because they do not require expensive dewatering equipment; as a result, nearly all of the newer installations have been designed for medium consistency operation. Delignification is limited to 40-50% to prevent pulp strength loss because oxygen lacks the selectivity needed for more complete delignification. The addition of a magnesium salt as a cellulose protector helps in this regard. Oxidized kraft pulping liquor is normally used as a source of the alkali needed to promote the reaction. Typical conditions are 2.5% NaOH, 30 minutes, 500 kPa (5 atm), 110°C at 27% consistency and 3% NaOH, 60 minutes, 500 kPa, 90°C at 12% consistency. Oxygen consumption is typically 2-3%.

Addition of oxygen to a first caustic extraction stage is usually achieved by dispersing oxygen in the pulp as it enters an upflow tower or preretention tube. An absolute oxygen pressure of 250 kPa, maintained for three minutes, is sufficient. Addition of 5 kg oxygen per ton of pulp allows the chlorine dioxide charge in a following stage to be reduced by 5 kg.

Ozone. Ozone bleaching has been the subject of laboratory and pilot plant studies for many years, but it remained uncommercialized until the announcement of the 1992 start-up of a full-scale plant at Union Camp's Franklin, Virginia, mill. The laboratory studies have shown that ozone rapidly and extensively delignifies chemical pulps over wide ranges of consistency and other conditions. The two major obstacles to commercialization have been

selectivity and cost. Because ozone is such a powerful oxidizing agent, it tends to be indiscriminate, so its application must be carefully controlled to prevent pulp strength loss. The cost is high because it must be generated on-site by passing pure, dry oxygen through a corona discharge, a process that consumes electrical energy and places high demands on the purification system for recycling unconverted oxygen in the spent ozone stream. Nevertheless, the growing demand for chlorine alternatives is likely to result in these problems being at least partially overcome, and ozone bleaching will soon be a commercial reality. The selectivity and cost problems probably preclude direct replacement of chlorine, as in the ZEDED sequence and favor combinations with other delignifying agents, as in the sequences OZED and O(DZ)ED. A likely scenario involves the use of ozone charges of less than 1%, high consistency, and ambient conditions.

Newer Developments. Research in progress points to the possible commercialization of several other chemical pulp bleaching technologies. These are chemical pretreatments to improve the selectivity of oxygen bleaching, enzymatic pretreatments to facilitate subsequent delignification, and recycling of bleach plant effluents. The first is best exemplified by the use of nitrogen dioxide pretreatment to extend the limit on oxygen delignification from 50% to 80% or perhaps higher. Although nitrogen dioxide does not itself remove appreciable amounts of lignin, it accelerates subsequent oxygen delignification reactions with the result that less cellulose degradation occurs for a given degree of delignification. Problems remain, but the establishment of the principle may lead to eventual commercial use of this or some other selectivity-improving chemical pretreatment. Enzymatic pretreatments that selectively remove hemicelluloses have been shown to result in major reductions in oxidant requirements for subsequent delignification; hemicellulose removal may facilitate lignin removal by enlarging pores or by disrupting lignin-carbohydrate linkages. Finally, recovery and recycle of bleach plant effluents are the subjects of considerable research. Environmental constraints on bleach plant discharges provide a growing incentive for this research, which also benefits from a full-scale mill closure experiment that lasted for several years at Great Lakes Forest Products in Thunder Bay, Ontario. One approach under investigation involves ultrafiltration of the effluent and incineration of the concentrate in a dedicated combustion unit.

MECHANICAL PULP

In recent years, there has been rapid development of high-yield pulping technology, including production of thermomechanical pulp (TMP) and chemithermomechanical pulp (CTMP). TMP is made by disk refining at elevated temperature and pressure. Under these conditions lignin softens, offering less resistance to fiber separation, and pulp of higher strength is obtained. CTMP carries lignin softening one step further by subjecting the wood chips to a mild chemical treatment, usually with sodium sulfite. Because little material is lost in these processes, the pulps have a very high lignin content. Consequently, it is not feasible to bleach them by removing all of the lignin as in chemical pulp bleaching. Instead, the lignin must be decolorized, and the process is sometimes referred to as brightening to distinguish it from lignin-removing bleaching methods. Only two brightening agents, hydrogen peroxide and sodium hydrosulfite (sodium dithionite), are of commercial importance.

Hydrogen Peroxide. Hydrogen peroxide is favored where high brightness is desired. Its effectiveness increases with increasing consistency, so it is normally applied at medium (12%) or high (25-30%) consistency. An important variable is pH, which must be sufficiently high to ensure partial dissociation of the peroxide to its active form, the perhydroxyl anion, but not so high as to result in color forming side reactions and excessive peroxide decomposition. An initial value of 10.5-11 is usually targeted. Decomposition can also be a problem within the optimum pH range, so sodium silicate (2-4%) and magnesium sulfate (0.05% as Epsom salt) are added to inactivate traces of catalytic transition metal ions, such as iron, manganese, and copper. For the same reason, the pulp may also be pretreated with a chelating agent, usually DTPA or EDTA. The bleaching is usually done in a tower at 40-60°C for 1-3 h, and peroxide applications of 1-4% are used. Alternatively, bleaching may be conducted by injecting the bleach liquor into the disk refiner where the pulp is made or by applying it to the pulp just prior to drying storage in partially dried (wet lap) form. Bleaching to high brightness requires high peroxide charges and unavoidably results in large amounts of residual peroxide in the spent bleach liquor. Where very high brightness is desired, as in some CTMP markets, multistage systems are employed to utilize the peroxide in the spent liquor. In one type, the pulp is prebleached in a first stage with spent liquor from the second stage.

Sodium Hydrosulfite. Reductive bleaching with sodium hydrosulfite is used when modest brightness gains are sufficient. An important consideration in applying hydrosulfite is its reactivity with oxygen; air must be excluded from the system to avoid loss of bleaching power. This is facilitated by operating at consistencies low enough

(3-4%) to ensure that air is not trapped in the pulp suspension. The effectiveness of hydrosulfite under these conditions is an advantage since it allows the bleaching to be conducted in available pulp storage vessels instead of a dedicated tower. Towers, nevertheless, are often used for the increased degree of control they provide. Temperature should be as high as possible and is usually maintained in the range 50-70°C for about 1 h. The pH should be close to 6.0. Brightness increases with increasing hydrosulfite charge up to about 1%, beyond which no further benefit is obtained. One recent development in hydrosulfite bleaching technology is the use of high-shear mixers to remove air and to mix the chemical with the pulp for bleaching at medium consistency. Another is in-refiner bleaching, which yields significantly higher brightness gains than the conventional tower process. Hydrosulfite is also sometimes used after peroxide in a two-stage process.

Hydrosulfite may be purchased as a proprietary formulation containing buffering and stabilizing agents, usually as a dry powder but sometimes as a solution. The powder is pyrophoric and should be kept dry to avoid the possibility of fires. Alternatively, solutions of sodium hydrosulfite may be generated on-site by using a purchased solution of sodium borohydride and sodium hydroxide to reduce sulfur dioxide.