BLEACHING AGENTS

1. Introduction

A bleaching agent is a material that lightens or whitens a substrate through chemical reaction. The bleaching reactions usually involve oxidative or reductive processes that degrade color systems. These processes may involve the destruction or modification of chromophoric groups in the substrate as well as the degradation of color bodies into smaller, more soluble units that are more easily removed in the bleaching process. The most common bleaching agents generally fall into two categories: chlorine and its related compounds (such as sodium hypochlorite) and the peroxygen bleaching agents such as hydrogen peroxide and sodium perborate. Reducing bleaches represent another category. Bleaching agents are used for textile, paper, and pulp bleaching as well as for home

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laundering. The textile industry is continuously under pressure to improve the environmental acceptability of its processes, and the related discharged effluents. The introduction of new enzyme-based technology to replace existing processes is thus particularly attractive. In processing natural fibers for textiles, the bleaching process is not only aimed at brightening the fibers, removing noncellulosic natural matter, eg, fats, waxes, pectines, proteins, and pigments (1,2), but is also directly related to subsequent wet processing operations such as dyeing, printing, and finishing (3). Whitening textiles is achieved traditionally by using various oxidizing or reducing agents at acidic or alkaline conditions, and at a wide range of temperatures. The desired whiteness level depends on the ultimate use of the fabrics. When higher level of whiteness is required it is necessary to perform a repeated oxidizing treatment.

Currently, hydrogen peroxide replaces almost entirely the traditional chlorine oxidizing agents (4,5). Accordingly, hydrogen peroxide precursors, such as perborates and percabonates, are major constituents of commercial detergents. Normally the bleaching agents are dosed in excess to the fibers, resulting in repeated washing to remove the residual oxidants, which are destructive to the proceeding processes. This method renders the bleaching process high in chemicals, water, energy, and time, as well as posing environmental hazard because of the discharged waste liquor. The introduction of a new, more environmentally friendly alternative enzyme-based technology to replace existing processes is therefore especially appealing.

2. The History of Bleaching

2.1. Textile Bleaching. There is evidence of chemical bleaching of cloth prior to 300 BC (6). Soda ash prepared from the burning of seaweed was used to clean the cloth followed by souring, ie, treatment with soured milk to neutralize the alkalinity remaining on the cloth. The cloth was then exposed to the sun to complete the bleaching process. Sun bleaching, which became known as crofting, occurred over a matter of weeks during which time the cloth was kept moist to enhance the bleaching process (7). During the eighteenth century, improvements were developed including the use of sulfuric acid in the souring process and the use of lime in the cleaning process, though crofting still required large tracts of primarily coastal land. With the onset of mechanized weaving, the production of cloth was outstripping the availability of land, which set the stage for the introduction of chemical bleaching.

Scheele, a Swedish chemist, discovered chlorine gas in 1784 and demonstrated its use in decolorizing vegetable dyes. Berthollet first produced solutions of hypochlorite by combining chlorine gas with alkalies and suggested using the gas for bleaching. A Scottish bleacher followed the suggestion and introduced chlorine into a bleach works in Glasgow. The efficiency of the process lead to its widespread use, though the low pH resulted in fabric damage and worker health problems. Two chemists, Valette and Tennant, developed chlorinated lime solutions that minimized these difficulties.

Tennant received a patent in 1799 for bleaching powder formed by the absorption of chlorine gas by dry hydrate of lime. Although this eliminated the need for on-site manufacture of chlorine, evidence suggests its use by bleachers caught on slowly. The bleaching powder was the chief source of textile bleaches over the next century and was the impetus for much of the early chemical and chemical engineering developments. Tropical bleach was developed by the addition of quicklime to bleaching powder to make a material suitable for use under tropical conditions. After World War I, technology for shipping liquid chlorine and caustic economically was developed allowing for the on-site manufacture of sodium hypochlorite solutions at the textile mills. As a result, use of bleaching powder diminished.

After World War I, other chlorine-based bleaches were developed. In 1921, the use of chlorine dioxide for bleaching fibers was reported followed by the development of the commercial process for large-scale production of sodium chlorite. In 1928, the first dry calcium hypochlorite containing 70% available chlorine was produced in the United States. This material largely replaced bleaching powder as a commercial bleaching agent.

Although hydrogen peroxide was prepared as early as 1818 by Thenard, the peroxides received little use as textile bleaches. Hydrogen peroxide was first prepared by the action of dilute sulfuric acid on barium peroxide, but later sodium peroxide and dilute acids were used. The prices of peroxides were high initially, and they found use only as a specialty chemical. Electrolytic methods in the 1920s allowed for the synthesis of less costly, strong ($\sim$30%) solutions of hydrogen peroxide. By 1930, hydrogen peroxide was being used to bleach cotton goods, wool, and silk on a limited scale. Shortly thereafter, the J-Box was developed by the FMC Corp. allowing for continuous bleaching of textiles with hydrogen peroxide (8). By 1940, 65% of all cotton bleaching was done with hydrogen peroxide.

2.2. Pulp Bleaching. The development of pulp bleaching parallels textile bleaching in many respects partially because early paper was generally made from rags. In the 1700s, sunlight was used to bleach paper. After the turn of the century, bleaching powder was used to whiten the rags used to make paper. During the nineteenth century, wood began to be used as a source of paper and sulfite pulping was developed. Although the Kraft process was discovered not long after, the sulfite process dominated for many years, since it yielded a whiter more easily bleached pulp. Calcium hypochlorite continued to be the bleaching agent used but multistage bleaching processes began to be employed. After World War I, compressed chlorine gas became available and its well-established properties as a delignifying agent ultimately resulted in its use in a chlorine-caustic extraction-hypochlorite (CEH) bleaching sequence. By the 1950s, chlorine dioxide generators were developed leading to the extensive use of this chemical as a bleaching agent particularly for the hard to bleach Kraft pulp. More recently peroxygens, particularly hydrogen peroxide, have been utilized (see PULP BLEACHING).

2.3. Household and Commercial Laundering. Prior to the turn of the twentieth century home bleaching in the United States was accomplished by the same method used by the ancient Romans and Gauls. Clothes were laundered in a mildly alkaline bath and then subjected to sunlight bleaching. In the period from 1910 to 1920, 5.25% sodium hypochlorite solutions were developed and distributed regionally in the United States. By the mid-1930s these solutions were available nationwide. This formula has remained essentially unchanged since its initial introduction. In the 1950s laundry products containing dry sources of hypochlorite were introduced into the United States. However, by the late 1960s the dry chlorine products had disappeared probably because of lower efficacy compared to liquid hypochlorite and fabric damage resulting from placement of the product on wet fabric. In Europe, laundry detergents containing sodium perborate as a bleaching agent were introduced in the early 1900s (9). The perborate dissolves during the laundering process and releases hydrogen peroxide. Sodium perborate continues to be heavily used in European laundry detergents because of the high (up to 95°C) wash temperatures. In the 1950s, laundry products containing sodium perborate were introduced in the United States. In the late 1970s, tetraacetylethylenediamine (TAED), a perborate activator, was introduced into European detergents. TAED with perborate generates peracetic acid in the wash, which is more effective than hydrogen peroxide. TAED is currently contained in $>50\%$ of European detergents (10). In the United States in 1982 a dry bleach containing diperoxydodecanedioic acid was test marketed but not expanded. In the late 1980s, a detergent product containing the perborate activator nonanoyloxybenzene sulfonate was introduced. This activator generates pernonanoic acid when combined with hydrogen peroxide generated from sodium perborate monohydrate.

Commercial laundries have used and continue to use sodium hypochlorite as the primary bleaching agent because of its whitening and disinfectant properties.

3. The Mechanism of Bleaching

Bleaching is a decolorization or whitening process that can occur in solution or on a surface. The color-producing materials in solution or on fibers are typically organic compounds that possess extended conjugated chains of alternating single and double bonds and often include heteroatoms, carbonyl, and phenyl rings in the conjugated system. The portion of molecule that absorbs a photon of light is referred to as the chromophore (Greek: *color bearer*). For a molecule to produce color, the conjugated system must result in sufficiently delocalized electrons such that the energy gap between the ground and excited states is small enough so that photons in the visible portion of the light spectrum are absorbed (see COLOR).

Bleaching and decolorization can occur by destroying one or more of the double bonds in the conjugated chain, by cleaving the conjugated chain, or by oxidation of one of the other moieties in the conjugated chain. The result of any one of the three reactions is an increase in the energy gap between the ground and excited states, so that the molecule then absorbs light in the ultraviolet region, and no color is produced. Bleaching may also increase the water solubility of organic compounds after reaction. Conversion of an olefin to a vicinal diol, eg, dramatically increases the polarity and consequently water solubility of the compound. A variety of bleaching agents can affect this transformation. The increased solubility allows actual removal of the bleached substance from a surface.

Chlorine bleaches react with more chromophores than oxygen bleaches. They react irreversibly with aldehydes, alcohols, ketones, carbon–carbon double bonds, acidic carbon–hydrogen bonds, nitrogen compounds, sulfur compounds, and aromatic compounds. Mixtures of products are usually formed because of the variety of active forms in equilibrium with each other (11). Also, many reactions occur in a series of steps, of which the first is usually ratelimiting. With hypochlorous acid, the first step often involves electrophilic addition to carbon–carbon double bonds to form chlorohydrins and epoxides. Or, it may involve electrophilic substitution of aromatic or acidic hydrogens by chlorine. Free-radical reactions are also possible. Nucleophilic addition also occurs with hypochlorite anion, which forms oxygenated products via the elimination of HCl. Aliphatic compounds usually react further to form acids, carbon dioxide, and ketones. Also, most carbon–carbon double bonds and carbon–carbon bonds with adjacent carbonyl or hydroxyl groups can be cleaved. Similar results are often obtained with chlorine dioxide. However, chlorine dioxide reacts with slightly fewer functional groups and often at slower rates than chlorine or hypochlorous acid. Chlorine dioxide also reacts by different mechanisms, which are generally less well understood. With some substrates the main products are chlorinated, but the percentage is usually less than with chlorine or hypochlorous acid (12–14).

The mechanism of bleaching of hydrogen peroxide is not well understood. It is generally believed that the perhydroxyl anion (HOO^-) is the active bleaching species since both the concentration of this anion and the rate of the bleaching process increase with increasing pH (15). Whereas the role of free-radical reactions in the bleaching process remains speculative, mechanisms involving heavy-metal catalyzed reactions are generally undesirable, since they often reduce the effective bleaching because of the rapid loss of peroxide and may also result in fabric damage if the metal is entrapped in the fabric (16). Hydrogen peroxide and other peroxygen compounds can destroy double bonds by epoxidation. This involves addition of an oxygen atom across the double bond usually followed by hydrolysis of the epoxide formed to 1,2-diols under bleaching conditions.

Peracids undergo a variety of reactions which result in bleaching. Peracids can add an oxygen across a double bond to give an epoxide, which can undergo further reactions including hydrolysis to give a vicinal diol. Peracids can oxidize aldehydes to acids, sulfur compounds to sulfoxides and sulfones, and nitrogen compounds to amine oxides, hydroxylamines, and nitro compounds (17). Peracids can also oxidize alpha-diketone compounds to anhydrides and ketones to esters. The protonated and deprotonated forms of the peracids are both effective bleaches. The protonated form acts as an electrophile whereas the deprotonated form is a nucleophilic oxidant.

Reducing agents are thought to work by reduction of the chromophoric carbonyl groups in textiles or pulp.

4. Chlorine-Containing Bleaching Agents

Chlorine-containing bleaching agents are the most cost-effective bleaching agents known. They are also effective disinfectants, and water disinfection is often the largest use of many chlorine-containing bleaching agents. They may be divided into four classes: chlorine, hypochlorites, *N*-chloro compounds, and chlorine dioxide.

The first three classes are called available chlorine compounds and are related to chlorine by the equilibria in equations 1–4. These equilibria are rapidly established in aqueous solution (18), but the dissolution of some hypochlorite salts and *N*-chloro compounds can be quite slow.

$$\mathrm{Cl_2\ (gas) \rightleftharpoons Cl_2\ (aq)} \tag{1}$$

$$\mathrm{Cl_2\ (aqueous) + H_2O \rightleftharpoons HOCl + H^+ + Cl^-} \tag{2}$$

$$\mathrm{HOCl \rightleftharpoons H^+ + OCl^-} \tag{3}$$

$$\mathrm{RR'NCl + H_2O \rightleftharpoons HOCl + RR'NH} \tag{4}$$

The total concentration or amount of chlorine-based oxidants is often expressed as available chorine or less frequently as active chlorine. Available chlorine is the equivalent concentration or amount of Cl_2 needed to make the oxidant according to equations 1–4. Active chlorine is the equivalent concentration or amount of Cl atoms that can accept two electrons. This is a convention, not a description of the reaction mechanism of the oxidant. Because Cl_2 only accepts two electrons as does HOCl and monochloramines, it only has one active Cl atom according to the definition. Thus the active chlorine is always one-half of the available chlorine. The available chlorine is usually measured by iodometric titration (19,20). The weight of available chlorine can also be calculated by equation 5.

$$\text{weight available chlorine} = 70.9 \times \text{moles of oxidant} \times \frac{\text{number active Cl atoms}}{\text{molecule}} \tag{5}$$

where 70.9 represents the mol wt of Cl_2 and moles of oxidant can be represented wt oxidant/mol wt of oxidant.

In solutions, the concentration of available chlorine in the form of hypochlorite or hypochlorous acid is called free-available chlorine. The available chlorine in the form of undissociated *N*-chloro compounds is called combined-available chlorine. Several analytical methods can be used to distinguish between free- and combined-available chlorine (20). Bleaches that do not form hypochlorite in solution like chlorine dioxide and nonchlorine bleaches can be characterized by their equivalent available chlorine content. This can be calculated from equation 5 by substituting the number of electrons accepted divided by two for the number of active chlorine atoms. It can also be measured by iodometric titration.

The actual form of an available chlorine bleach in solution must be determined from equations 1–4. The equilibrium constants for equations 2 and 3 are $3.94 \times 10^{-4}\ M^2$ (21) and $2.88 \times 10^{-8}\ M$ (22) at 25°C, respectively. Thus, above pH $9.5 > 99\%$ of the available chlorine is present as hypochlorite ions. The ratio of hypochlorous acid to hypochlorite ion increases with decreasing pH until pH 5.5, below which $<1\%$ of the available chlorine will be hypochlorite ions. Below pH 6, Cl_2 may be present. Its amount increases with decreasing pH

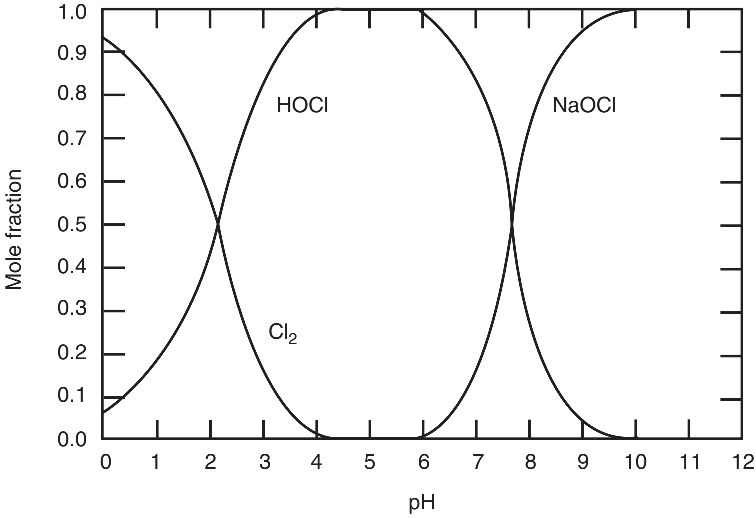


Fig. 1. Distribution of 0.5 wt% available chlorine with equimolar chloride at 25°C in a closed system.

and increasing total available chlorine. With an available chlorine concentration of 0.1%, Cl_2 begins to appear ~pH 4 and becomes dominant ~pH 2.5. At an available chlorine concentration of 10%, Cl_2 appears ~pH 6, and becomes dominant ~pH 4.5. Figure 1 shows the distribution of available chlorine species as a function of pH in an aqueous solution of 0.5% available chlorine. Other species that may be present in insignificant amounts are Cl_3^-; from Cl_2 (aq) and H_2OCl^+ and Cl_2O from HOCl (11).

With *N*-chloro compounds, the species in solution also depends on their individual hydrolysis constants as shown in equation 4. Those with larger constants allow a higher hypochlorite concentration, which usually gives stronger bleaching because *N*-chloro compounds are weaker oxidants than hypochlorite (see CHLORAMINES AND BROMAMINES). Although *N*-chloro compounds react quickly with other *N*-compounds and may remove some stains faster than hypochlorite (23), the undissociated *N*-chloro compound usually serves as a reservoir to replenish hypochlorite as it is consumed. This reduces reactivity compared to the higher hypochlorite concentration required to deliver the same amount of available chlorine (24–26). Stability of the available chlorine may also be improved (27,28). Even when the *N*-chloro compound completely dissociates at the use concentration, it can reduce the hypochlorite concentration in a concentrated solution or product. This may reduce the damage done by spills, improve stability, or allow the use of a wider variety of ingredients. *N*-Chloro compounds may also be formed *in situ* as when *N*-compounds are used in dry compositions with active chlorine compounds to scavenge free hypochlorite to protect other materials (29).

Solutions of available chlorine bleaches decompose on standing at a rate that depends on the conditions described below. Hypochlorous acid [7790-92-3] and hypochlorite anions decompose according to equations 6 and 7 (30,31).

$$3\,\mathrm{HOCl} \longrightarrow \mathrm{HClO_3} + 2\,\mathrm{HCl} \tag{6}$$

$$3\,\mathrm{OCl^-} \longrightarrow \mathrm{ClO_3^-} + 2\,\mathrm{Cl^-} \tag{7}$$

The solutions are most stable >pH 11 where the decomposition rate is nearly independent of pH. In this region, the decomposition rate has a second-order dependence on the concentration of hypochlorite. It also increases with increasing ionic strength. Thus concentrated solutions decompose much faster than dilute solutions. Because of an unusually high activation energy, the decomposition rate increases greatly with temperature. Nevertheless, solutions with less than ~6% available chlorine and a pH > 11 have acceptable long-term stability below ~30°C.

Below pH 11, the decomposition rate becomes dependent on pH and the mechanism becomes more complicated. The rate increases greatly as the pH decreases from 11 to 7 where the rate reaches a maximum. As the pH decreases from 7 to 3, the rate decreases. Below ~pH 3 the rate becomes reasonably slow but still considerably faster than at pH 11. The mechanisms are not well known, and they may be different in each of these pH ranges. In all cases, the decomposition rate increases greatly with temperature and with a second- or higher-order dependence on the concentration of hypochlorous acid and/or hypochlorite.

Decomposition also occurs by equation 8, which can usually be ignored unless it is catalyzed by transition-metal ions (32,33):

$$2\,\mathrm{OCl^-} \longrightarrow \mathrm{O_2} + 2\,\mathrm{Cl^-} \tag{8}$$

Even very small amounts of transition-metal ions like cobalt, nickel, and copper cause rapid decomposition. They form reactive intermediates that can decrease the stability of oxidizable compounds in the bleach solution and increase the damage to substrates. Hypochlorite is also decomposed by ultraviolet (uv) light (34,35). Acidic solutions also lose available chlorine by the reverse of equations 1 and 2.

Commercially important solid available chlorine bleaches are usually more stable than concentrated hypochlorite solutions. They decompose very slowly in sealed containers. But most of them decompose quickly as they absorb moisture from air or from other ingredients in a formulation. This may release hypochlorite that destroys other ingredients as well.

4.1. Chlorine. Except to bleach wood pulp and flour, chlorine [7782-50-5] itself is rarely used as a bleaching agent. Chlorine is almost always first converted into one of the bleaching agents described, and they are almost always used at a pH where $\mathrm{Cl_2}$ is not present. However, it has been the practice to use acid chlorination where $\mathrm{Cl_2}$ is the active species in the first step of pulp bleaching. Since chlorine reacts primarily by chlorination, large amounts of chlorinated organic by-products are formed (36). Environmental concerns about discharging these by-products in waste effluents are rapidly changing this process (37–39).

4.2. Hypochlorites. *Sodium Hypochlorite.* The principal form of hypochlorite produced is sodium hypochlorite [7681-52-9], NaOCl. It is invariably made and used as an aqueous solution and is usually prepared by the chlorination of sodium hydroxide solutions as shown in equation 9, though other bases such as sodium carbonate can be used (40).

$$Cl_2 + 2\,NaOH \rightleftharpoons NaOCl + NaCl + H_2O \tag{9}$$

Chlorine gas is usually used, but electrolysis of alkaline salt solutions in which chlorine is generated *in situ* is also possible and may become more important in the future. The final pH of solutions to be sold or stored is always adjusted >11 to maximize stability. The salt is usually not removed. However, when the starting solution contains >20.5% sodium hydroxide some salt precipitates as it is formed. This precipitate is removed by filtration to make 12–15% NaOCl solutions with about one-half of the normal amount of salt. Small amounts of such solutions are sold for special purposes. Solutions with practically no salt can be made by reaction of high purity hypochlorous acid with metal hydroxides.

A 5–6% sodium hypochlorite solution is sold for household purposes, of which the largest use is in laundry. Solutions of 10–15% NaOCl are sold for swimming pool disinfection, institutional laundries, and industrial purposes. Solutions of various strengths are used in household and industrial and institutional (I & I) cleaners, disinfectants, and mildewcides. A small amount is used in textile mills. Sodium hypochlorite is also made on site with 30–40 g/L available chlorine for pulp bleaching, but its use is decreasing in order to reduce chloroform emissions (see CHLORINE OXYGEN ACIDS AND SALTS).

Calcium Hypochlorite. The principal form of solid hypochlorite produced commercially is calcium hypochlorite [7778-54-3], $Ca(OCl)_2$. It decomposes rapidly and exothermically gives off oxygen and chlorine monoxide gases when heated >175°C. It also reacts vigorously or explosively with oxidizable materials. The most common form contains 6–12% water and 65% available chlorine. The water reduces the risk of self-sustained decomposition because of organic contaminants or ignition. The older variety contains about 1% water and 70–74% available chlorine. Both forms also contain sodium chloride [7647-14-5] and small amounts of calcium hydroxide [1305-62-0], calcium chloride [10043-52-4], calcium chlorate [10137-74-3], and calcium carbonate [471-34-1]. They are made by chlorination of hydrated lime (calcium hydroxide) in a way that minimizes the amounts of unwanted salts. The resulting product contains much fewer insoluble materials and is more stable than bleaching powder.

The largest use of calcium hypochlorite is for water treatment. It is also used for I & I and household disinfectants, cleaners, and mildewcides. Most of the household uses have been limited to in-tank toilet bowl cleaners. In areas where chlorine cannot be shipped or is otherwise unavailable, calcium hypochlorite is used to bleach textiles in commercial laundries and textile mills. It is usually first converted to sodium hypochlorite by mixing it with an aqueous solution of sodium carbonate and removing the precipitated calcium carbonate. Or, it can be dissolved in the presence of sufficient sodium tripolyphosphate to prevent the precipitation of calcium salts. However, calcium hypochlorite is not usually used to bleach laundry and textiles because of problems with insoluble inorganic calcium salts and precipitation of soaps and anionic detergents as their calcium salts.

Bleach Liquor. Bleach liquor or lime bleach liquor is an aqueous solution of calcium hypochlorite and calcium chloride. It typically contains 30–35 g/L of available chlorine, though it may be as high as 85 g/L. It has been used in pulp bleaching, when it can be made more cheaply than sodium hypochlorite. It is prepared on site by chlorinating lime solutions.

Bleaching Powder and Tropical Bleach. Bleaching powder [64175-94-6], also known as chlorinated lime and chloride of lime, is an indefinite, complex mixture of calcium hypochlorite, calcium hydroxide, calcium chloride, and their hydrates. The proportions of these species vary with the manufacturer as does the available chlorine, which usually ranges between 24 and 37%. It is usually made by chlorinating slightly moist hydrated lime (calcium hydroxide). It has also been made by chlorinating a slurry or solution of calcium chloride (41). Bleaching powder readily decomposes in moist air through the absorption of water and carbon dioxide. Its stability can be improved by adding calcium oxide. Since this is needed especially in hot, humid climates, such mixtures are known as tropical bleach, super tropical bleach, or stabilized tropical bleach. They typically contain 15–30% available chlorine.

Historically, bleaching powder and tropical bleach were significant sources of available chlorine but very little are used today. This is because of the greater availability of sodium hypochlorite solutions and the development of calcium hypochlorite. They are still used to sanitize fields, drainage ditches, and reservoirs where its insoluble portion is not important. And, they are important sources of available chlorine within some less developed tropical countries.

Dibasic Magnesium Hypochlorite. This salt $Mg(OCl)_2 \cdot 2Mg(OH)_2$, [11073-21-5], is safer than calcium hypochlorite because of its higher thermal stability and its endothermic rather than exothermic decomposition. Its preparation as a solid with 50–58% available chlorine is patented (42,43) but not sold commercially.

Lithium Hypochlorite. Commercial lithium hypochlorite [13840-33-0], LiOCl, is a solid with ~35% available chlorine. It is made from concentrated solutions of sodium hypochlorite and lithium chloride. It consists of 30% lithium hypochlorite and various other salts (44).

Lithium hypochlorite is used in I & I laundry detergents and I & I dry laundry bleaches. Like sodium hypochlorite, it does not precipitate soaps and other anionic detergents. However, lithium hypochlorite is an expensive source of available chlorine and not much is used for bleaching. Its principal use is as a shocking agent for swimming pool disinfection.

Chlorinated Trisodium Phosphate. Chlorinated trisodium phosphate [11084-85-8] is a crystalline complex of hydrated trisodium orthophosphate and sodium hypochlorite that releases hypochlorite when mixed with water. Its formula is $(Na_3PO_4 \cdot 11H_2O)_4 \cdot NaOCl$. Commercial products have 3.5–3.7% available chlorine. They are probably a mixture of phosphate salts, and they contain some sodium chloride.

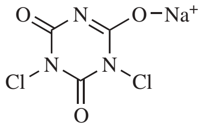
The use of chlorinated trisodium phosphate is declining. It has been largely replaced by chlorinated isocyanurates in powdered abrasive cleansers and automatic dishwash detergents to reduce cost, improve performance, or comply with restrictions on the use of phosphates. Some chlorinated trisodium phosphate is still used in commercial laundries and in disinfectant cleaners.

Hypochlorous Acid. Hypochlorous acid [7790-92-3] solutions are made for immediate use as chemical intermediates from chlorine monoxide or in bleaching and water disinfection by adjusting the pH of hypochlorite solutions. Salt-free hypochlorous acid solutions have been economically made from steam and chlorine (45). These solutions may have sufficient stability at 0°C to be sold for industrial use.

Oxidation of Chlorides. Hypochlorite can also be formed by the *in situ* oxidation of chloride ions by potassium peroxymonosulfate [25482-78-4] (46). Ketones like acetone catalyze the reaction (47). The triple salt of potassium peroxymonosulfate is a stable powder that has been combined with chloride salts and sold as toilet bowl cleaners. Bromides can be used in place of chlorides to form hypobromites, and such combinations are used to disinfect spas and hot tubs.

Hypobromites. The chemistry of hypobromite is similar to hypochlorite. It reacts faster than hypochlorite and gives better bleaching at higher pH and lower temperatures. It also decomposes according to equations 6 and 7 much faster than hypochlorite. The most stable solutions decompose quickly and must be freshly prepared. This can be done by adding a bromide salt to a hypochlorite solution, since hypochlorite oxidizes bromide to hypobromite. Usually a catalytic amount of bromide is used since much of it will be regenerated as the hypobromite is reduced during bleaching (48). Dry compositions containing a bromide salt and a solid available chlorine compound can also be used (49). A few *N*-bromo compounds are also available.

4.3. *N*-Chloro Compounds. *Chlorinated Isocyanurates.* The principal solid chlorine bleaching agents are the chlorinated isocyanurates. The one used most often for bleaching applications is sodium dichloroisocyanurate dihydrate [51580-86-0] with 56% available chlorine. It is the most water-soluble, the fastest to dissolve, and the least hazardous. It has good stability and compatibility with other dry ingredients. Anhydrous sodium [2893-78-9] (1) and potassium [2244-21-5] salts with 63 and 59% available chlorine are also available. The potassium salt is less soluble in water and is claimed to have the best stability in dry products containing other ingredients (50). Trichloroisocyanuric acid [87-90-1] (2) with 90% available chlorine is the most economical and the one used most often for water disinfection. Not much is used for bleaching because it dissolves slowly and has poor stability in dry products containing other ingredients. It also decomposes with moisture to give off explosive nitrogen trichloride gas.



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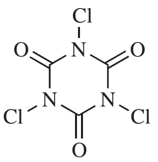

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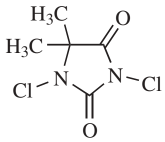

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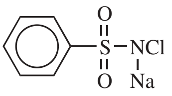
Halogenated Hydantoins. These are stable solids with limited use as bleaches. They dissolve too slowly to use in household laundry and automatic dishwashing. 1,3-Dichloro-5,5-dimethylhydantoin [118-52-5] (3) is sold with 65–75% available chlorine. It is used as a bleach in hospital and other industrial laundries and in disinfectant cleaners. Some 1-bromo-3-chloro-5,5-dimethylhydantoin [6079-88-2] is also used. It is a more effective bleach and disinfectant at lower temperatures and higher alkalinities than 1,3-dichloro-5,5-dimethylhydantoin because it hydrolyzes to hypobromite.

Other N-Chloro Compounds. Sodium *N*-chlorobenzenesulfonamide (chloramine B) [127-52-6] (4), sodium *N*-chloro-*p*-toluenesulfonamide (chloramine T) [127-65-1] (5), *N*-chlorosuccinimide [128-09-6] (6), and trichloromelamine [12379-38-3] (7) have also had minor roles as bleaching agents.



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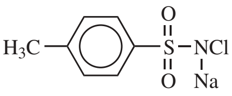

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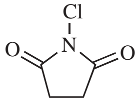

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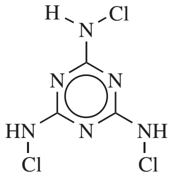


(7)

They are mainly sold as disinfectants, because they display poor bleaching as a result of low hydrolysis constants or poor solubility. *N*-Chloro compounds with low hydrolysis constants like chloramine T can be used to boost the bleaching of peroxide laundry bleaches (51–54). The bleaching remains inferior to using sodium hypochlorite laundry bleach, however. Tetrachloroglycoluril [776-19-2] (55) sodium trichlorometaphosphimate [67651-15-14] (56), sodium *N*-chloroimidodisulfonate [67700-32-7] (57), 1,3-dichlorotetrahydroquinazoline-2,4-dione [23767-45-5] (58,59), and *N*-chlorophenylbiquanidino compounds (60,61) have been unsuccessfully marketed as bleaching agents. Many other *N*-chloro compounds have been patented as bleaching agents, the most notable are mono- [17172-27-9] and dichlorosulfamic acid [17085-87-9] (62–64).

4.4. Chlorine Dioxide. Chlorine dioxide [10049-04-4], ClO_2, is a gas that is more toxic than chlorine. It can explode at concentrations $>10\%$ in air. The liquid boils at 11°C but explodes above −40°C. It can be stored and transported as its octahydrate if kept frozen, but almost all chlorine dioxide is made on site for immediate use. Large amounts for pulp bleaching are made by several processes (65,66) in which sodium chlorate [7775-09-9] is reduced with chloride, methanol, or sulfur dioxide in highly acidic solutions by complex reactions. For most other purposes, chlorine dioxide is made from sodium chlorite [7758-19-2]. Acidic solutions of sodium chlorite are oxidized by chlorine as in equation 10:

$$2\,NaClO_2 + Cl_2 \longrightarrow 2\,NaCl + 2\,ClO_2 \tag{10}$$

Hypochlorous acid can also be used, but the reaction is slower. Chlorine dioxide is also made by adding acid to sodium chlorite solutions by the overall reaction in equation 11:

$$5\,NaClO_2 + 4\,HCl \longrightarrow 4\,ClO_2 + 5\,NaCl + 2\,H_2O \tag{11}$$

Some chlorine and chlorate also form through competing reactions. Chlorine dioxide is also evolved from mixtures of powdered sodium chlorite and acidic clays or alumina.

The reactivity of acidified chlorite solutions is reduced for bleaching some textiles by adding compounds like polyamines, pyrophosphates, and hydrogen peroxide that suppress the formation of chlorine dioxide (12). Another method is to buffer the solution at pH 5–6 to reduce the rate of chlorine dioxide formation. Hydrolysis of anhydrides and esters or oxidation of alcohols can be used to slowly generate acids to promote chlorine dioxide formation (67). Aldehydes also promote chlorine dioxide generation from neutral chlorite solutions, but the effect is greater than simply lowering the pH as they oxidize to acids (68).

Chlorine dioxide is usually used in aqueous solution. It is a weaker oxidant than hypochlorite. Unlike chlorine it does not react with water to form hypochlorite or with amines to form *N*-chloro compounds. Thus chlorine dioxide is easily removed from solutions by passing air through the solution or its headspace. Chlorine dioxide solutions decompose by equation 12:

$$2\,ClO_2 + 2\,NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O \qquad (12)$$

This reaction is very slow in acid but rapid above pH 10. Chlorine dioxide solutions are also decomposed by light.

The biggest use of chlorine dioxide is in bleaching wood pulp. In some mills, much of the chlorine and hypochlorite has been replaced by chlorine dioxide to reduce the amount of chlorinated by-products. Chlorine dioxide is also used to bleach textiles, flour, and edible fats and oils.

5. Peroxygen Compounds

Peroxygen compounds contain the peroxide linkage (–O–O–) in which one of the oxygen atoms is active. This activity, referred to as active oxygen (AO), is measured by the oxidation of iodide to iodine under acidic conditions or by a ceric sulfate titration (69). Active oxygen content, usually expressed as a percent, is the atomic weight of active oxygen divided by the molecular weight of the compound (eq. 13):

$$\text{active oxygen, }\% = 100 \times \text{number of active oxygens} \times 16\ \text{mol wt of compound}$$

5.1. Hydrogen Peroxide.

Hydrogen peroxide [7722-84-1] is one of the most common bleaching agents (see HYDROGEN PEROXIDE). It is the primary bleaching agent in the textile industry, and is also used in pulp, paper, and home laundry applications. In textile bleaching, hydrogen peroxide is the most common bleaching agent for protein fibers, and is also used extensively for cellulosic fibers.

Pure hydrogen peroxide has an active oxygen content of 47%. It is the least expensive source of active oxygen commercially available. Moreover, it is a liquid, making it convenient for many bleaching applications. Hydrogen peroxide is usually sold in solutions containing 30–35%, 50% or 65–70 wt % of the active material. More concentrated solutions (80–85%, 90%) are available in limited quantities. Concentrated solutions of hydrogen peroxide are hazardous and must be handled with extreme care (70).

Hydrogen peroxide is a very weak acid and in aqueous solutions only dissociates slightly (eq. 14); $K_a = 1.78 \times 10^{-12}$. Undissociated hydrogen peroxide is relatively stable, and for this reason all commercial products are adjusted to an acid pH (71).

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \tag{14}$$

A considerable amount of energy is liberated when hydrogen peroxide undergoes decomposition to oxygen and water (eq. 15): $\Delta H_{25°C} = -94.64$ kJ/mol (-22.62 kcal/mol); activation energy = 209 kJ/mol (50 kcal/mol).

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}\,O_2 \tag{15}$$

This decomposition may be considered a self-oxidation and occurs most rapidly in basic solutions. Decomposition of hydrogen peroxide is also greatly accelerated in the presence of heavy metals and easily oxidizable substances (72). The presence of low concentrations of heavy metals (such as Fe and Cu) in hydrogen peroxide can increase the rate of decomposition by many orders of magnitude over the entire pH range for typical uses. Therefore, commercial hydrogen peroxide solutions are stabilized with additives that provide protection against decomposition (73–77). Typically these additives are metal chelating agents that bind free metal ions and significantly reduce the catalytic rate of decomposition.

Hydrogen peroxide bleaching is performed in alkaline solution where part of the hydrogen peroxide is converted to the perhydroxyl anion (eq. 14). The perhydroxyl anion is generally believed to be the active bleaching species and its concentration in solution increases with hydrogen peroxide concentration, alkalinity, and temperature (78). The alkaline agents most commonly used to generate HO_2^- are caustic soda, carbonates, silicates, pyrophosphates, and polyphosphates. Better bleaching is obtained at these alkaline conditions by increasing the temperature and by adding stabilizers to prevent the uncontrolled decomposition reactions of hydrogen peroxide. Common stabilizers include silicates, pyrophosphates, and polyaminocarboxylates. These stabilizers may be different from those used to stabilize commercial acidic hydrogen peroxide (15).

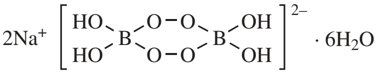
As a bleaching agent, hydrogen peroxide is much less effective than chlorine or hypochlorite; however, it does have several advantages over these bleaching agents. Hydrogen peroxide causes less textile fiber damage, is much gentler on fabric dyes, and does not have a strong odor. Attempts have been made to increase the bleaching power of hydrogen peroxide-based laundry bleaches by the addition of heavy-metal catalysts (79–83). The effectiveness of these systems remains controversial and these catalysts have not been incorporated into commercial products.

5.2. Solid Peroxygen Compounds. Hydrogen peroxide reacts with many compounds, such as borates, carbonates, pyrophosphates, sulfates, silicates, and a variety of organic carboxylic acids, esters, and anhydrides to give peroxy compounds or peroxyhydrates. A number of these compounds are stable solids that hydrolyze readily to give hydrogen peroxide in solution.

Perborates. Sodium perborate [7632-04-4] is the most widely used solid peroxygen compound. Commercially, it is available as a tetrahydrate [10486-00-7] and a monohydrate [10322-33-9]. The tetrahydrate is produced by treating a borax solution with hydrogen peroxide and sodium hydroxide:

$$Na_2B_4O_7 + 2\ NaOH + 4\ H_2O_2 + 11\ H_2O \longrightarrow 4\ NaBO_3 \cdot 4\ H_2O \tag{16}$$

The tetrahydrate has the structure (8) (84):



(8)

It has good stability and can be used in formulations with many compounds without serious loss of active oxygen. The monohydrate is made by dehydration of the tetrahydrate. The active oxygen contents of the tetrahydrate and monohydrate are 10.5 and 16.0%, respectively. The tetrahydrate is the perborate salt most commonly used in bleaching applications (85). However, as consumer trends move toward more concentrated products, monohydrate is growing in demand because of its higher AO content (86). Because sodium perborate has much greater stability than sodium hypochlorite, it can be formulated into a wide variety of products, including detergents. In the United States, perborates are used in all-fabric bleach formulations, detergents, denture cleaners, tooth powders, and other special cleaners. Sodium perborate is used extensively in Europe in detergent formulations.

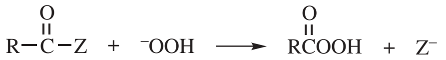
Sodium Carbonate Peroxyhydrate. Sodium carbonate peroxyhydrate [15630-89-4], which contains about 14 wt% of active oxygen, has the composition $2Na_2CO_3 \cdot 3H_2O_2$. A white, free-flowing solid, it generally can be used in all applications where perborate is used. Despite the fact that sodium carbonate peroxyhydrate has a greater rate of dissolution than sodium perborate tetrahydrate, the latter is usually favored for its good storage stability and better compatibility with the various materials used in formulations (87).

Peroxymonosulfate. Peroxymonosulfuric acid (Caro's acid) [7722-86-3], the peroxygen product of hydrogen peroxide and sulfuric acid, is a powerful oxidizing agent; however, because of its instability, it is hazardous (88). It is commercially available in Europe but not in the United States. The salt, potassium permonosulfate [25482-78-4] is commercially available under the trade name Oxone. This monopersulfate compound is a white solid having a satisfactory shelf life and an active oxygen content of ~4.5%. It is a triple salt with the composition $2KHSO_5 \cdot K_2SO_4 \cdot KHSO_4$. Oxone is used as a bleaching agent and in several other applications where a solid peroxygen source is required; however, the extent of its use is limited.

5.3. Peracids.

Peracids are compounds containing the functional group −OOH derived from an organic or inorganic acid functionality. Typical structures include $CH_3C(O)OOH$ derived from acetic acid and $HOS(O)_2OOH$ (peroxymonosulfuric acid) derived from sulfuric acid. Peracids have superior cold water bleaching capability versus hydrogen peroxide because of the greater electrophilicity of the peracid peroxygen moiety (89–91). Lower wash temperatures and phosphate reductions or bans in detergent systems account for the recent utilization and vast literature of peracids in textile bleaching (17,92).

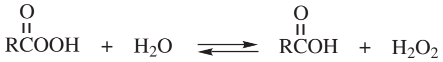
Peracids can be introduced into the bleaching system by two methods. They can be manufactured separately and delivered to the bleaching bath with the other components or as a separate product. Peracids can also be formed *in situ* utilizing the perhydrolysis reaction shown in equation 17.



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}Z + {}^{-}OOH \longrightarrow R\overset{O}{\overset{\|}{C}}OOH + Z^{-}} \qquad (17)$$

R can be a variety of structures. The leaving group is Z^{-} and is typically the conjugate base of a weak acid whose pK_a can range from 5 to 20 (93). The hydrogen peroxide is typically incorporated into the bath by adding a solid source of peroxide such as sodium percarbonate or the mono- or tetrahydrate of sodium perborate (93).

Peracid Analysis. Peracid concentrations can be measured in a product or in the bath by use of a standard iodide/thiosulfate titration (69). With preformed peracids or peracids formed via perhydrolysis care must be exercised to minimize the interference of hydrogen peroxide, present intentionally as a component of the perhydrolysis reaction or as a result of the hydrolysis of the peracid (94,95) as shown in equation 18.



$$\mathrm{R\overset{O}{\overset{\|}{C}}OOH + H_2O \rightleftharpoons R\overset{O}{\overset{\|}{C}}OH + H_2O_2} \qquad (18)$$

This is typically accomplished by cooling the titration solution with ice, determining the blank, and titrating rapidly. Another method utilizes determination of the total peroxide and peracid content by use of a ceric sulfate titration to measure hydrogen peroxide followed by a iodide/thiosulfate titration to measure total active oxygen (69).

Peracid Classification. Peracids can be broadly classified into organic and inorganic peracids, based on standard nomenclature. The limited number of inorganic peracids has required no subclassification scheme (9). However, the tremendous number of new organic peracids developed (17) has resulted in proposals for classification. For example, a classification scheme based on liquid chromatography retention times and critical micellization constants (CMC) of the parent acids has been proposed (96). The parent acids are used because of the instability of the peracids under chromatographic and micellization measurement conditions. This classification scheme is shown in Table 1.

The technique used to classify the peracids is artificial with respect to bleaching, but the classification of a peracid does relate to its location in the bleaching bath microenvironment. Hydrophilic peracids are quite water soluble and as such they are located in the bulk phase and their bleaching performance is the result of random collisions with the fabric surface (9). Since collisional frequency is increased at higher temperature the hydrophilic peracids are useful in high temperature washing conditions. The inorganic peracids are exclusively of the hydrophilic type. Hydrophobic peracids are similar in structure and behavior

Table 1. **Classification of Peracids**

Peracid type	Retention time[a] of parent acid	CMC	Typical structures
hydrophilic	<5 min	>0.5 *M*	peracetic, perpropionic, perbenzoic acids[b]
hydrophobic (surface active)	na	<0.5 *M*	[c]
hydrotropic	>5 min	none, or >0.5 *M*	[c]

[a] Chromatographic conditions: elution with 50:50 methanol/water solvent at the rate of 1.5 mL/min through a DuPont Zorbax ODS column using a Waters R-401 Refractive Index Detector.
[b] That is, in equations 17 and 18 R = CH_3, CH_2CH_3, or C_6H_5, respectively.
[c] See Figure 2.

to common detergent surfactants because they possess a hydrophilic head group [−C(O)OOH] and a hydrophobic tail [$CH_3(CH_2)_n$−]. These peracids have a defined CMC and as such are likely to be located in micelles (9,97). The ability of these peracids to partition to an interface make them more suitable for cold water washing than hydrophilic peracids (98,99). At cooler temperatures improved stain removal by the hydrophobic bleaches versus the hydrophilic bleaches has been demonstrated. No reports of the hydrotropic peracid bleach microenvironment locale have been published, but because of their oily character and based on Table 1 they are likely dissolved into the detergent micelle.

5.4. Peracid Precursor Systems. Compounds that can form peracids by perhydrolysis are almost exclusively amide, imides, esters, or anhydrides (17). Two compounds were commercially used for laundry bleaching as of 1990. Tetraacetylethylenediamine [10543-57-4] is utilized in >50% of western European detergents (10). The perhydrolysis reaction of this compound is shown in equation 19. TAED generates two moles of peracid and one mole of diacetylethylenediamine per mole of imide (100).

$$(CH_3\overset{O}{\overset{\|}{C}})_2NCH_2CH_2N(\overset{O}{\overset{\|}{C}}CH_3)_2 + 2\,H_2O_2 \longrightarrow 2\,CH_3\overset{O}{\overset{\|}{C}}OOH + CH_3\overset{O}{\overset{\|}{C}}NHCH_2CH_2NH\overset{O}{\overset{\|}{C}}CH_3 \qquad (19)$$

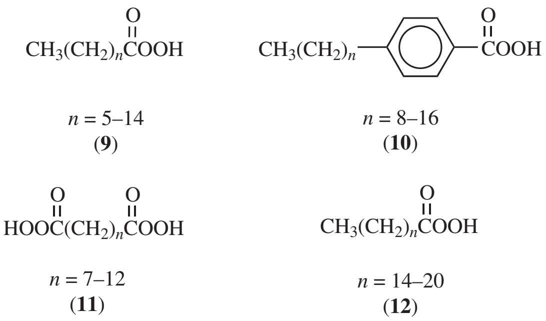
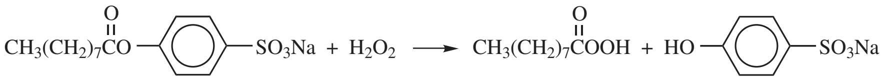


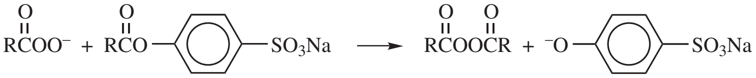
Fig. 2. Typical peracids; see Table 1. Compounds (9) and (10) are hydrophobic; (11) and (12) are hydrotropic.

The perhydrolysis reaction could theoretically continue to give four moles of peracid per mole of TAED but stops at this stoichiometry because of the substantial increase in the conjugate acid pK_a of the leaving group going from an amide (p$K_a = 17$) to an amine (p$K_a = 35$) (101,102). Nonanoyloxybenzene sulfonate (NOBS) [101482-85-3] is used in detergent products in the United States and Japan. The NOBS perhydrolysis reaction is shown in equation 20 (103).



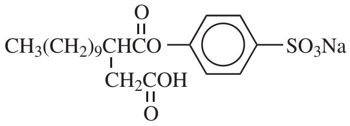
(20)

The NOBS system undergoes an additional reaction that forms a diacyl peroxide as a result of the nucleophilic attack of the peracid anion on the NOBS precursor as shown in equation 21. This undesirable side reaction can be minimized by the use of an excess molar quantity of hydrogen peroxide (98,103) or by the use of shorter dialkyl chain acid derivatives. However, the use of these acid derivatives also appears to result in less efficient bleaching. The dependence of the acid group on the side product formation is apparently the result of the proximity of the newly formed peracid to unreacted NOBS in the micellar environment (91). A variety of other peracid precursor structures can be found (104–125).

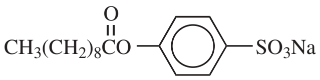


(21)

The pK_a of the leaving group and the hydrophobe chain length can dramatically affect the efficiency of the perhydrolysis reaction. Additionally, the structure of the acid portion of the precursor can affect the yield and sensitivity of the reaction to pH. The mono-4-hydroxybenzenesulfonic acid ester of α-decylsuccinic acid (13) undergoes extremely efficient perhydrolysis at much lower pH values than other peracid precursors, eg, decanoyloxybenzene sulfonate (14). This may be because of the neighboring group participation of the adjacent carboxylate as shown in Table 2 (122).



(13)



(14)

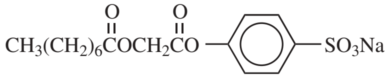
Electronic effects within the acid portion of the precursor have also been utilized for enhanced reactivity. The 4-hydroxybenzenesulfonate ester of

Table 2. **Effect of Alpha-Carbonyl Group on Peracid Yield**

Compound	Molecular formula[a]	pH	Peracid yields %
13	$C_{20}H_{30}O_7S$	9.5	97
14	$C_{16}H_{24}O_5S$	9.5	26

[a] Of the sulfonic acid.

octanoyloxyacetic acid, 15, undergoes efficient perhydrolysis at lower pH values because of the activation of the susceptible carbonyl by the beta-oxygen of the hydrophobic tail (107).

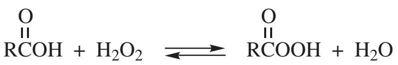


(**15**)

Attempts have also been made to reduce the odor associated with the peracid in the home laundry. Use of a precursor that generates the peracid of a fatty acid can result in an objectionable odor in the wash bath (113). This odor is exacerbated by the higher pK_a of the peracid versus its parent acid resulting in a greater proportion of the peracid in the unionized and therefore less water-soluble form. To mitigate this circumstance, functionalization of the fatty tail typically alpha to the carbonyl has been utilized (119). The modifications include alpha-chloro and alpha-methoxy substituents on the parent acid portion of the precursor ester.

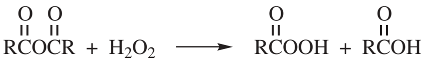
The peracid precursors can be susceptible to hydrolysis or perhydrolysis in the solid state particularly when incorporated into a detergent product that is exposed to high humidity conditions (125). To minimize the loss of precursor over time the material can be incorporated into granules to minimize the surface area to volume ratio, which minimizes storage instability. A variety of granulation techniques have been described in the literature of which extrusion and agglomeration have been commercialized (126–138). A limited number of references also discuss the incorporation of a precursor into a liquid matrix that contains either hydrogen peroxide or an insoluble source of hydrogen peroxide such as perborate (139,140).

5.5. Preformed Peracids. Peracids can be generated at a manufacturing site and directly incorporated into formulations without the need for *in situ* generation. Two primary methods are utilized for peracid manufacture. The first method uses the equilibrium shown in equation 22 to generate the peracid from the parent acid.



$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH} + \mathrm{H_2O_2} \rightleftharpoons \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOH} + \mathrm{H_2O} \qquad (22)$$

The equilibrium is shifted by removal of the water (141) or removal of the peracid by precipitation (142,143). Peracids can also be generated by treatment of an anhydride with hydrogen peroxide to generate the peracid and a carboxylic acid.



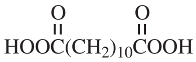
$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R} + \mathrm{H_2O_2} \longrightarrow \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOH} + \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH} \qquad (23)$$

The latter method typically requires less severe conditions than the former because of the labile nature of the organic anhydride (94,144). Both of these reactions can result in explosions and significant precautions should be taken prior to any attempted synthesis of a peracid (94). For solid peracids the reaction mixture can be neutralized with sodium hydroxide and the resulting filtercake washed with water. In the case of the sulfuric acid mediated reaction, the peracid has sodium sulfate incorporated in the cake (142). The water of hydration present in the sodium sulfate is desirable to prevent detonation or deflagration of the solid peracid when isolated in a dry state (94,145,146).

The water of hydration, particularly that incorporated in sodium sulfate decahydrate, however, can cause instability when the peracid–sulfate blend is subjected to elevated temperatures. To mitigate this problem materials known as exotherm control agents have been incorporated into peracid formulas. These materials release their water only when conditions occur that could lead to detonation or deflagration. Magnesium sulfate heptahydrate, magnesium sulfate–sodium sulfate tetrahydrate, and boric acid each release water near 100°C (145,147). The release of the water prevents the propagation of the decomposition of the peracid by removing heat via evaporation (147). These materials are incorporated into the peracid composition at concentrations up to equal weight by weight to the peracid.

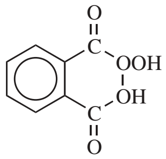
The peracid–exotherm control agent mixtures can be granulated using a variety of techniques common in the industry, including agglomeration. As with peracid precursors, the surface area to volume ratio can impact the stability of the peracid. Particles are thus made as large as possible to maintain stability (148).

Two solid organic peracids have been utilized in textile bleaching products. Diperoxydodecanedioic acid, 16, [66280-55-5], a hydrotropic peracid, and the magnesium salt [78948-87-5] of monoperoxyphthalic acid, 17, [2311-91-3], a hydrophilic peracid, were contained in bleaching products for a short period of time (149).



$$\mathrm{HOO\overset{O}{\overset{\|}{C}}(CH_2)_{10}\overset{O}{\overset{\|}{C}}OOH}$$

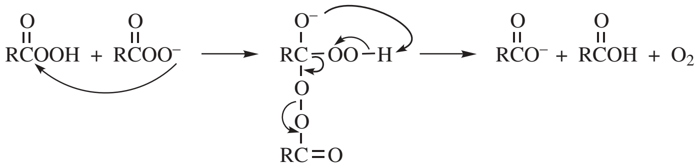
(16)



(17)

Peracids are also available as aqueous solutions that contain the peracid in equilibrium with hydrogen peroxide and the parent acid. Peracetic acid [79-21-0] is commercially available as a 40% solution in dilute acetic acid. The water and dilution of the peracid make these solutions easier to handle than their solid counterparts, but they still require careful handling and protection from heat.

Peracid Decomposition. Peracids, whether preformed or formed *in situ* via the perhydrolysis reaction, are susceptible to decomposition in an aqueous bleaching bath. The decomposition is caused by the occurrence of one of four reactions. The peracid can decompose as a result of oxidation of the bleachable material. Transition metals present even at extremely low concentration in the bath from the incoming water can decompose the peracid catalytically (150,151). To minimize this effect, metal-sequestering agents have been proposed to prevent the degradation of the peracid in solution (150,151). Peracids can also hydrolyze to the parent acid and hydrogen peroxide because of the large excess of water present in the aqueous bleaching bath. This is generally a kinetically slow process (94). A final decomposition mechanism involves the reaction of 2 mol of peracid generating 2 mol of parent acid and 1 mol of oxygen.



(24)

The reaction involves the nucleophilic attack of a peracid anion on the unionized peracid giving a tetrahedral diperoxy intermediate that then eliminates oxygen giving the parent acids. The observed rate of the reaction depends on the initial concentration of the peracid as expected in a second-order process. The reaction also depends on the structure of the peracid (specifically whether the peracid can micellize) (9). Micellization increases the effective second-order concentration of the peracid because of the proximity of one peracid to another. This effect can be mitigated by the addition of an appropriate surfactant, which when incorporated into the peracid micelle, effectively dilutes the peracid, reducing the rate of decomposition (9,97).

6. Reducing Bleaches

The reducing agents generally used in bleaching include sulfur dioxide, sulfurous acid, bisulfites, sulfites, hydrosulfites (dithionites), sodium sulfoxylate formaldehyde, and sodium borohydride. These materials are used mainly in pulp and textile bleaching (see SULFUR COMPOUNDS; BORON COMPOUNDS).

6.1. Sulfur Dioxide, Sulfites, and Bisulfites. Sulfur dioxide [7446-09-5] and its derivatives have been used to bleach textiles since earliest times. Sulfur dioxide is a gas formed by burning sulfur in air. Besides being an important bleaching agent in the pulp and paper industry, sulfur dioxide is also integral to some processes for chlorine dioxide, sodium hydrosulfite, and sodium sulfite. Sulfur dioxide is used in both Kraft and mechanical pulp processes, and it is unique in that its bleaching effect is independent of pH over the range 3–10 (152). When SO_2 is dissolved in water, it yields a complex mixture given the trivial name sulfurous acid [7782-99-2] (H_2SO_3), which contains SO_2, H_3O^+, $S_2O_5{}^{2-}$, and $HSO_3{}^-$. The composition of the mixture depends on the concentration of the sulfur dioxide in the water, the pH, and the temperature (153). Although sulfurous acid does not exist in the free state, it forms stable salts (the neutral sulfite, $SO_3{}^{2-}$, and the hydrogen sulfite or bisulfite $HSO_3{}^-$) which are good reducing agents (eqs. 25 and 26).

$$2\,SO_3^{2-} + O_2 \longrightarrow 2\,SO_4^{2-} \tag{25}$$

$$HSO_3^- + Cl_2 + 2\,OH^- \longrightarrow HSO_4^- + 2\,Cl^- + H_2O \tag{26}$$

Sodium sulfite [7757-83-7], which is used in pulp and paper bleaching, is usually produced by the reaction of sulfur dioxide with either caustic soda or soda ash.

$$SO_2 + 2\,NaOH \longrightarrow Na_2SO_3 + H_2O \tag{27}$$

$$SO_2 + Na_2CO_3 \longrightarrow Na_2SO_3 + CO_2 \tag{28}$$

Dithionites. Although the free-dithionous acid, $H_2S_2O_4$, has never been isolated, the salts of the acid, in particular zinc [7779-86-4] and sodium dithionite [7775-14-6] have been prepared and are widely used as industrial reducing agents. The dithionite salts can be prepared by the reaction of sodium formate with sodium hydroxide and sulfur dioxide or by the reduction of sulfites, bisulfites, and sulfur dioxide with metallic substances such as zinc, iron, or zinc or sodium amalgams, or by electrolytic reduction (154).

$$2\,HSO_3^- + SO_2 + Zn \longrightarrow ZnSO_3\downarrow + S_2O^{2-}{}_4 + H_2O \tag{29}$$

Aqueous solutions of dithionite are not stable in the presence of oxygen, low pH, or elevated temperatures. The decomposition of dithionite occurs by the following equation:

$$2\,S_2O^{2-}{}_4 + H_2O \longrightarrow 2\,HSO_3^- + S_2O_3^{2-} \tag{30}$$

Both sodium dithionite and zinc dithionite are produced commercially, though the uses of this latter salt have declined because of the regulatory constraints on pollution of water by zinc. The zinc salt is used under those conditions of pH and temperature where the sodium dithionite would be unstable. The principal applications of these compounds are in bleaching of mechanical pulp and in dyeing, printing, and stripping in the textile industry. A derivative of sodium dithionite is sodium sulfoxylate formaldehyde, which is prepared by the reaction of formaldehyde with the dithionite. Its applications are like those of dithionite except that it is less reactive and more stable thermally. When the sulfoxylate is used, a pH range of 3.2–3.5 produces the best results. For both the dithionite salts and sulfoxylate, the higher the temperature, the greater the reducing strength. The sulfoxylates can be used at temperatures as high as 100°C.

The principal bleaching applications of sodium dithionite are in the bleaching of mechanical or CTM pulps and the bleaching of kaolin clays for use as filler for fine paper. Other applications include the bleaching of glues, gelatin, soap, and food products. A significant new application for dithionite is in the bleaching of recycled paper.

7. Enzymes for Bleaching in the Textile Industry

7.1. Bleaching of Textile Substrates.

Enzymes are used for bleaching purposes in the textile industry for decolorization of dyehouse effluents, bleaching of released dyestuff, and inhibiting dye transfer (155–158). However, only a few enzymes, ie, xylanses, cellulases, and proteases (159–169), exert some bleaching effect on the textile substrate itself. Enzymatic systems suitable for bleaching of textile materials are further classified as: enzymes for production of the bleaching agent and enzymes acting directly on the textile substrate.

Biogeneration of Hydrogen Peroxide for Bleaching. Hydrogen Peroxide Generation with Free Glucose Oxidase. The most common bleaching agent, hydrogen peroxide, may be produced enzymatically by glucose oxidase (EC 1.1.34), which catalyzes the conversion of β-D-glucose in aqueous solutions in the presence of oxygen as electron acceptor (170). Similar enzymatic systems are used as constituents in detergent formulations to generate controlled rates of hydrogen peroxide (171,172).

The gluconic acid formed in the enzymatic reaction acts as a chelator for metal ions, thus, addition of peroxide stabilizing agents may be avoided. Activation of the enzymatically produced peroxide is performed at elevated temperature and in the alkaline medium. Aeration is crucial for the production of hydrogen peroxide as it increases considerably the activity of glucose oxidase. However, enzyme concentration has to be optimized, as higher concentrations speed up reaction rate; but at additional costs.

One of the drawbacks of biobleaching is inactivation of free enzymes, which is caused by foam formation in the aerated solution, by shear forces acting on the enzyme molecule during stirring (173) or by high concentration of hydrogen peroxide formed during the reaction. Another problem is that the amount of enzymatically produced peroxide that is required is twofold that of the standard bleaching amount (174). This might be due to the added glucose, which is assumed to be acting as a stabilizer or as a substrate for oxidation, thus competing with the cotton fiber and lowering the bleaching rate. Another possible reason for the increased required amount of peroxide is the elevated process temperature this temperature cause protein denaturation and facilitates hydrophobic fabric–enzyme interaction (175), thereby preventing effective bleacing rates. The latter problems are avoided by using immobilized instead of free enzyme.

An example for a process with free glucose oxidase is a closed-loop enzymatic desizing–scouring–bleaching process. Using residual starch desizing baths containing glucose as an additional source for substrate in the enzymatic peroxide generation is an economically attractive option. Advantageously, the entire process is carried out in the residual desizing bath, so no fresh water is added, this results in considerable water savings (174). The combined desizing and bleaching process is suitable when there is no need for very high level of whiteness, since the high contamination of the reused desizing–scouring–bleaching liquor decreases the bleaching effect of the peroxide.

Hydrogen Peroxide Generation with Immobilized Glucose Oxidase. One reason that a bleaching process using enzymatically produced peroxide is not yet commercial is that the enzymes are still quite expensive. Immobilization of the enzymes provides long-term application of the enzyme at lower process cost. Immobilization accounts for easy recovery and recycling, reudced enzyme dosage, and continuous operations.

Enzymes have been immobilized on various insoluble carriers for a large number of applications inlcuding research, diagnostics, food, pharmaceutical, medical, and industrial uses. The methods of immobilization include adsorption, ionic, and covalent binding, which is most appropriate when the enzymes are used under extreme conditions when high stability is required. When choosing a support for enzyme immobilization for industrial application, the most important criteria are the stability of the carrier and the cost.

Glucose oxidases have been immobilized on polyethylene-*g*-acrylic acids graft copolymer membranes (176), silicone supports (177) silk fibroin membranes (178) activated carbon, glass, collagen, polycarbonate, polyurethane, polypyrrole films, and cellulose (179). The main application is as electrochemical biosensors (180). For textile bleaching purposes (181) glucose oxidase is covalently immobilized on an inexpensive, commercially available porous alumina carrier using glutaraldehyde as cross-linking agent. Alumina is recommended as carrier in the pH range of pH 5–11 (182). The pH range provides the slightly acidic environment required for the enzymatic reaction of glucose oxidase and glucose.

Immobilized glucose oxidase shows good operational stability in the textile bleaching process, and is reusable for at least three cycles without significant loss of activity. Sufficient amount of peroxide for bleaching can be produced with relatively low enzyme concentration. As a whole, the rate of peroxide generation from immobilized glucose oxidase is nearly twofold lower compared with the free enzyme. Immobilized enzyme increases slightly the level of whiteness of the fabrics bleached compared with the free enzyme, by eliminating the effect of the protein in the bleaching liquor. The recycling capacity of the enzyme might be improved by appropriate stabilization techniques. A prolonged storage, however, has a clear adverse influence on the enzyme activity.

When using immobilized glucose oxidase higher enzyme loadings on the support do not produce higher levels of hydrogen peroxide (183,184), as the amount of bound enzyme does not necessarily correlate with the recovered activity (185). Binding the glucose oxidase onto the support results normally in significant alterations of enzyme conformation and microenvironment (186). Moreover, fluoresence microscopy studies show (187) that the immobilized enzyme is in the outer shell of the alumina carrier pellets, and that not all the pore volume is efficiently accessible to immobilization. Thus, diffusion constraint, which is known as one of the most dominant effects, influences the performance of the immobilized enzyme (188).

Bleaching of Textiles Chloroperoxidases. The haloperoxidases (EC 1.11.1.10) form a class of heme-containing enzymes capable of oxidizing halides in the presence of hydrogen peroxide to the corresponding hypohalous acid (189–193). If an appropriate nucleophile is present, a reaction occurs with formation of hypohalous acid, whereby bleaching takes place at lower than the conventional bleaching temperature and pH. This type of bleaching reduces damage to fiber and avoids the use of bleaching auxiliaries. A recent patent reported the use of haloperoxidases for textile treatment (194).

The mechanism of chloroperoxidase catalyzed chlorination reactions is considerably controversial. Some reports favor the direct transfer of the chlorine atom from the enzyme to the substrate (191), others insist on the involvement of free oxidized chlorine intermediate Cl_2 in a reaction catalyzed by chloroperoxidases (195). The differenece between these two reaction pathways is based on the rate of oxidation of the chloride to its respective molecular species and the rate of enzymatic chloination of the substrates (191). In a haloperoxidase-catalyzed halogenation reactions both hypohalous acid intermediate and hydrogen peroxide are reactive toward the enzyme, and can cause significant inactivation at high concentrations (194). High halide concentration might also inhibit the enzyme.

Chloroperoxidases application alone cannot replace chemical bleaching (196). The enzymatic pretreatment might be an alternative to the repeated conventional bleaching process or a way to reduce significantly the peroxide dosage in subsequent chemical bleaching. However, this enzymatic system might face problems with environmental restrictions regarding the absorbable organic halogens by-products in industrial effluents.

Bleaching of Textiles with Laccases. Laccases (EC 1.10.3.2) are multicopper enzymes that catalyze the oxidation of a wide range of inorganic substances using oxygen as an electron acceptor (197). The oxidation of a reducing substrate involves typically formation of a free (cation) radical after the transfer of a single electron to laccase (198). Laccases have found various biotechnological and environmental applications eg, removal of toxic compounds from polluted effluents through oxidative enzymatic coupling of the contaminants leading to insoluble complex structures, or as biosensors for phenols (199–204). Laccases have been extensively used in bleaching of craft pulp in delignification and demethylation (197,204–208). Capability of laccases to act on chromophore compounds suggested their application in industrial decolorization processes (155–157,208,209). However, these enzymes have not yet been used for bleaching of textiles despite promising experimental results. Apparently, laccase pretreatment alone does not improve the whiteness of the textile material; moreover, it generates color. However, after hydrogen peroxide bleaching, the whiteness of the enzymatically pretreated fabrics reaches whiteness index enhancement comparable with the whiteness achieved in two consecutive peroxide bleaching runs (210). It is well documented that laccase produces colored substances when suitable substrate is present (211). Although the nature of the coloring matter, in the case of cotton, is not fully characterized, it is believed to be related to nitrogen-free flavone pigments. These compounds are based on the flavonoid skeleton, which is a three-ring molecule, two of them aromatic, connected by a heterocyclic central ring. These pigments are normally removed only after oxidizing bleaching; however, they might be subjected to laccase-mediated oxidation. Pectin substances, remaining in the scoured cotton, might be a substrate for laccase as well. The mechanism of laccase bleaching action is not fully understood; however, experiments support the hypothesis that the enzyme transforms the cellulose coloring matter into other colored compounds, which are more easily oxidized by peroxide. The advantage of the enzymatic process over conventional bleaching is in terms of reduced time, energy, and chemicals consumption.

In a different process, the bleaching is carried out at elevated temperature (1–5 min at 100°C), after impregnation of the fabrics with laccase on foulard. These short-time pretreatments render the enzymatic approach suitable for continuous operations.

7.2. Enzymes for Treatment of Textile Bleaching Effluents.

Removal of Residual Peroxide in Bleaching Effluents with Free Catalases. The washing process after bleaching consumes large amounts of water, since any residual hydrogen peroxide has to be removed to avoid problems in subsequent dyeing processes. Minor modifications of the dye molecule can result in color loss (212,213). The demands to reduce water consumption by reducing or eliminating the washing cycle after bleaching while ensuring good reproducibility of dyeing can be met by application of catalases. Catalase is widely distributed enzyme in nature and well known for its ability to catalyze the conversion of hydrogen peroxide to water and gaseous oxygen. It has found numerous applications in food science, industrial food production, and medical any analytical fields (214,215). Commercial products containing catalase for textile applications are also available. These have been used to decompose residual hydrogen peroxide in fabric prior to dyeing, and are normally applied after draining the bleaching bath and refilling it with fresh water (216). A new, unconventional dyeing technique, ie, dyeing within the bleaching bath, is now implemented (217). In this technique, the bleaching bath, containing the fabric, is treated directly with catalase to destroy the residual hydrogen peroxide, and then being reused for reactive dyeing.

There are two particular limitations to this approach: the low of stability of the catalase at high temperature and pH, and the influence of the bleaching bath components on enzyme efficiency and on dye uptake. Though hydrogen peroxide is completely destroyed by the enzyme, the bleaching bath formulation caused unacceptable color changes of the dyed fabrics. Temperature increase causes significant changes in the structure of catalase, which is related to thermal unfolding and denaturing of the enzyme (175). Hence, color changes of the dyed textiles are attributed to the temperature-dependent dye–enzyme precipitation as well as to the bleaching bath composition. Bath liquors contain various substances that are extracted from the cotton, eg, oils and waxes, pectins, proteins, organic acids, mineral, and natural coloring matter. Optimizing the dyeing process, ie, dye, salt, alkali, and enzyme concentrations are the key to successful dyeing in the bleaching bath, and thereby to a considerable water and energy conservation gained by avoiding an extensive washing cycle after bleaching.

Removal of Residual Peroxide in Bleaching Effluents with Immobilized Catalases. Major problems in use of catalases arise from the high temperature and alkalinity of the bleaching and washing liquors. The sensitivity of catalytically active protein structures to high temperatures, extreme pH, and other denaturing causes is one of the most important factors in the commercialization and industrial application of enzymes (218,219). In general, stabilization of the enzymes can be achieved in several ways: screening for stable ones such as thermophiles and extremophiles, chemical modification, protein engineering, immobilization, or stabilizing additives use (220–223). Interactions between dye and protein renders the use of soluble catalase inappropriate (175,224) alternatively, immobilized catalase can be used (219,225). Covalent binding of catalase to the support improves the resistance of the enzyme to inactivation presumably by restricting the protein unfolding process as a result of both intra- and intermolecular cross-linking.

Immobilized catalase is used for hydrogen peroxide degradation in column and tank reactor. Column reactor with substrate recirculation is more appropriate due to faster decompostion of the peroxide. For both types, reactor inhibition of the enzyme occurs when substrate concentrations exceeds 1 M. Dyeing in the recycled water provides a greater consistency of color than that obtained by using the free enzyme.

8. Economic Aspects

The chemicals used for bleaching have a variety of uses outside of bleaching technology. As a consequence, detailed information regarding production of these materials for bleach use is limited.

Sodium hypochlorite accounts for 92% of global use of the hypochlorite bleaches. Calcium hypochlorite accounts for the remaining 8%.

Residential use of sodium hypochlorite breaks down into the following categories: laundry bleaching (80%); sanitizers (18%); and residential pool and spa treatment (2%). Industrial uses are as follows: industrial and municipal water treatment (45%); commercial and municipal swimming pool treatment (33%); commercial laundry bleach (5%); liquid dishwashing detergent (5%); textile bleaching (4%), chemical (4%), and miscellaneous (4%).

Household demand in 2002 was 540×10^6 gal, projection for 2006 is 569×10^6 gal. Industrial demand in 2002 was 278×10^6 gal. The projected demand for 2002 is 292×10^6 gal. Growth is expected to continue at the rate of 1.3% through 2006 (226).

Calcium hypochlorite is used as a shock treatment in swimming pools. Shock treatments boost the chlorine levels in pools. Swimming pool treatment accounts for 75% of calcium hypochlorite use, the remaining is used for municipal and industrial water treatment.

Demand projected for 2003 is ~79,000 tons (227). Demand is expected to grow in the United States at the rate of 2–4%. Demand in Japan is expected to rise ~ 1% (228). Displacement of calcium hypochlorite by chlorinated isocyanurates has leveled off. Consumption of the chlorinated isocyanurates in 2000 was 180,000 t (229).

9. Health and Safety Factors

Much new information regarding the toxicities of sodium chlorite and sodium hypoclorite has become available, primarily as a result of safety concerns about chlorinated drinking water. In general, human population studies and animal bioassays have not found an association between exposure to these compounds and an increased risk of cancer, reproductive, or teratogenic effects.

The International Agency for Research on Cancer has concluded that there is inadequate evidence for the carcinogenicity of sodium hypochlorite in animals, and that sodium hypochlorite is not classifiable as to its carcinogenicity in humans (group 3).

The current OSHA PEL for perchlorates as nuisance dust is 15 mg/m^3. The California groundwater standard is 18 μg/L (230).

Hydrogen peroxide is a confirmed carcinogen and is moderately toxic by inhalation, ingestion, and skin contact. OSHA PEL TWA is ppm no as is the ACG IH TLV (231).

Sulfur dioxide OSHA PEL TWA and ACGIH TLV TWA are both 2ppm, STEL. ACGIH notes not classifiable as a human carcinogen (231).

10. Uses

10.1. Laundering and Cleaning.

Home and Institutional Laundering. The most widely used bleach in the United States is liquid chlorine bleach, an alkaline aqueous solution of sodium hypochlorite. This bleach is highly effective at whitening fabrics and also provides germicidal activity at usage concentrations. Liquid chlorine bleach is sold as a 5.25% solution and 1 cup provides 200 ppm of available chlorine in the wash. Liquid chlorine bleaches are not suitable for use on all fabrics. Dry and liquid bleaches that deliver hydrogen peroxide to the wash are used to enhance cleaning on fabrics. They are less efficacious than chlorine bleaches but are safe to use on more fabrics. The dry bleaches typically contain sodium perborate in an alkaline base whereas the liquid peroxide bleaches contain hydrogen peroxide in an acidic solution. Detergents containing sodium perborate tetrahydrate are also available.

The worldwide decreasing wash temperatures, which decrease the effectiveness of hydrogen peroxide based bleaches, have stimulated research to identify activators to improve bleaching effectiveness. Tetraacetylethylenediamine is widely used in European detergents to compensate for the trend to use lower wash temperatures. TAED generates peracetic acid in the wash in combination with hydrogen peroxide. TAED has not been utilized in the United States where one activator nonanoyloxybenzene sulfonate (NOBS) has been commercialized and incorporated into several detergent products. NOBS produces pernonanoic acid when combined with hydrogen peroxide in the washwater and is claimed to provide superior cleaning to perborate bleaches.

In industrial and institutional bleaching either liquid or dry chlorine bleaches are used because of their effectiveness, low cost, and germicidal properties. Dry chlorine bleaches, particularly formulated chloroisocyanurates, are used in institutional laundries.

Hard Surface Cleaners and Cleansers. Bleaching agents are used in hard surface cleaners to remove stains caused by mildew, foods, etc, and to disinfect surfaces. Disinfection is especially important for many industrial uses. Alkaline solutions of 1–5% sodium hypochlorite that may contain surfactants and other auxiliaries are most often used for these purposes. These are sometimes thickened to increase contact times with vertical surfaces. A thick, alkaline cleaner with 5% hydrogen peroxide is also sold in Europe. Liquid abrasive cleansers with suspended solid abrasives are also available and contain ~1% sodium hypochlorite. Powdered cleansers often contain 0.1–1% available chlorine and they may contain abrasives. Sodium dichloroisocyanurate is the most common bleach used in powdered cleansers, having largely replaced chlorinated trisodium phosphate. Calcium hypochlorite is also used. Dichloroisocyanurates are also used in effervescent tablets that dissolve quickly to make cleaning solutions. In-tank toilet cleaners use calcium hypochlorite, dichloroisocyanurates, or *N*-chlorosuccinimide to release hypochlorite with each flush to prevent stains from forming. One powdered toilet bowl cleaner uses potassium peroxymonosulfate and sodium chloride to generate hypochlorite in *in situ*.

Automatic Dishwashing and Warewashing. The primary role of bleach in automatic dishwashing and warewashing is to reduce spotting and filming by breaking down and removing the last traces of adsorbed soils. They also remove various food stains such as tea. All automatic dishwashing and warewashing detergents contain alkaline metal salts or hydroxides. Liquids, gels, and slurries contain 1–3% sodium hypochlorite. Powders and tablets almost always use 1–4% sodium dichloroisocyanurate dihydrate. Trichloroisocyanurate and the once popular chlorinated trisodium phosphate are also used. A few powders use sodium percarbonate or sodium perborate. They are less effective than chlorine bleaches, but this is largely overcome by increased amounts of alkaline metal salts or hydroxides. Enzymes (qv) also work with peroxygen bleaches but are deactivated by chlorine bleaches. Sodium hypochlorite or chloramine T are also used as sanitizers in the last rinse of low temperature warewashing.

10.2. Textile Bleaching. Many textiles are bleached to remove any remaining soil and colored compounds before dyeing and finishing (see TEXTILES). Bleaching is usually preceded by washing in hot alkali to remove most of the impurities in a process called scouring. Bleaching is usually done as part of a continuous process, but batch processes are still used. Not all fabrics are bleached, but natural fibers and their blends usually are. To minimize fiber damage, a minimum of bleaching agent is used. Making white and lightly colored fabrics requires the most bleaching. Bleaching conditions vary widely, depending on the equipment, the bleaching agent, the type of fiber, and the amount of whiteness required for the end use (67,68,232–235).

Cotton and Cotton–Polyester. Cotton is the principal fiber bleached today, and almost all cotton is bleached. About 80–90% of all cotton and cotton–polyester fabric is bleached with hydrogen peroxide. With hydrogen peroxide the fabric does not need to be scoured before bleaching and there is little risk of overbleaching. Typically, bleaching with 0.3–0.6% hydrogen peroxide solutions at pH 10.5–11.5 is done for 1–3 h at 90–95°C. The time can be reduced to 2–15 min by increasing the severity of the scouring step, impregnating the fabric with larger amounts of hydrogen peroxide, and using steam to attain temperatures of 95–100°C. In pressurized vessels at 130–145°C the time is reduced to 0.75–2 min. In order to save energy, some plants combine scouring and bleaching with hydrogen peroxide into a single step. Other plants use cold bleaching in which the textiles are scoured, bleached with sodium hypochlorite, and then bleached with hydrogen peroxide at room temperature for 4–5 h with a catalyst (236), or for 12–16 h without a catalyst. With all processes, bleaching with hypochlorite or chlorine dioxide may precede peroxide bleaching when white or lightly colored textiles are desired.

In the past, sodium hypochlorite solution (called chemic by textile workers) was the most commonly used bleach. Some is still used today because of its lower cost and better whitening ability than hydrogen peroxide. However, bleaching with hypochlorite needs to be carefully controlled to prevent fiber damage. Also, when only hypochlorite bleach is used, the fabrics need to be well scoured first to remove soils that consume hypochlorite. Otherwise higher hypochlorite concentrations and longer bleaching times are needed, which increase the risk of fabric damage. Protein soils may also form chloramines that cause color reversion. Solutions of 0.1–0.5% sodium hypochlorite are typically used at pH 10–11.5 for 0.5–4 h at 20°C or for 15–30 min at 40–50°C. The fabric is then bleached with hydrogen peroxide, or it is washed in a solution of a reducing agent (antichlor), such as bisulfite or sulfur dioxide, to remove residual hypochlorite and chloramines.

Sodium chlorite is also used to bleach some cotton and cotton–polyester fabrics. Unlike peroxide and hypochlorite, which only whiten the cotton portion of cotton–polyester blends, sodium chlorite also whitens polyester. However, the polyester portion usually does not need to be whitened. Sodium chlorite whitens better than hydrogen peroxide, does not damage fibers, and can be used with unscoured fabrics. However, it is more expensive, more corrosive to metals, and more hazardous than peroxide or hypochlorite. Typically, solutions of 0.1–3% sodium chlorite with sufficient dihydrogen phosphate and formic acid to give pH 3.8–4.2 are used at 80–95°C for 1–6 h. In a room temperature process, fabric is treated overnight with a neutral solution of sodium chlorite that is activated by formaldehyde. Minor bleaching agents that are used in a manner similar to hydrogen peroxide are sodium peroxide [1313-60-6], sodium perborate, and sodium percarbonate [20745-24-8]. Perborate or percarbonate are most frequently used as additives to scouring solutions in place of a separate bleaching step when a fully whitened fabric is not needed.

Other Cellulosics. Rayon is bleached similarly to cotton but under milder conditions since the fibers are more easily damaged and since there is less colored material to bleach. Cellulose acetate and triacetate are not usually bleached. They can be bleached like rayon, except a slightly lower pH is used to prevent hydrolysis. The above fibers are most commonly bleached with hydrogen peroxide. Linen, flax, and jute require more bleaching and milder conditions than cotton, so multiple steps are usually used. Commonly, an acidic or neutral hypochlorite solution is followed by alkaline hypochlorite, peroxide, chlorite, or permanganate, or a chlorite step is done between two peroxide steps. A one-step process with sodium chlorite and hydrogen peroxide is also used.

Synthetic Fibers. Most synthetic fibers are sufficiently white and do not require bleaching. For white fabrics, unbleached synthetic fibers with fluorescent whitening agents are usually used. When needed, synthetic fibers and many of their blends are bleached with sodium chlorite solutions at pH 2.5–4.5 for 30–90 min at concentrations and temperatures that depend on the type of fiber. Solutions of 0.1% peracetic acid are also used at pH 6–7 for 1 h at 80–85°C to bleach nylon.

Wool and Silk. Wool must be carefully bleached to avoid fiber damage. It is usually bleached with 1–5% hydrogen peroxide solutions at pH 8–9 for several hours at 40–55°C or at pH 5.5–8 for 20–60 min at 70–80°C. Silk is bleached similarly, but at slightly higher temperatures.

Wool with dark pigmented fibers is treated with ferrous sulfate, sodium dithionite, and formaldehyde before it is bleached with hydrogen peroxide. The ferrous ions are absorbed by the dark pigments where they increase the bleaching done by the peroxide.

Wool may also be bleached with reducing agents, usually after bleaching with hydrogen peroxide. This is the normal practice with wool blends. In the reducing step, 0.2–0.5% sodium dithionite solutions are often used at pH 5.5–7 for 1–2 h at 45–65°C. Faster bleaching is obtained with zinc hydroxymethanesulfinate[24887-06-7] below pH 3 and >80°C.

The ancient process of stoving is still occasionally used to bleach wool and silk with sulfur dioxide. In this process, wet fabrics are hung in chambers of burning sulfur or sulfur dioxide gas for at least 8 h. The fabrics are then washed with sodium sulfite to remove excess sulfur dioxide. Fabric so treated may have unpleasant odors, and the original color eventually returns, but the process is simple and inexpensive.

10.3. Bleaching of Other Materials. *Hair.* Hydrogen peroxide is the most satisfactory bleaching agent for human hair. Solutions containing 3–4% hydrogen peroxide, available from drug stores and supermarkets, are commonly used. In beauty shops, more rapid bleaching is desired and a 5–6% solution is used. Ammonium hydroxide is usually the source of alkalinity in both systems (see COSMETICS; HAIR PREPARATIONS).

Fur. Fur is bleached to permit dyeing to the desired shade. The coloring matter in fur is usually bleached using hydrogen peroxide stabilized with sodium silicate. For difficult to bleach dark hairs it is necessary to add a step using a reducing agent with a catalyst such as ferrous sulfate. The formula and procedures are the same as those used for wool.

Foodstuffs, Oils. Sulfur dioxide is used to preserve grapes, wine (qv), and apples; the process also results in a lighter color. During the refining of sugar (qv), sulfur dioxide is added to remove the last traces of color. Flour can be bleached with a variety of chemicals including chlorine, chlorine dioxide, oxides of nitrogen, and benzoyl peroxide [94-36-0]. Bleaching agents such as chlorine dioxide or sodium dichromate [10588-01-9] are used in the processing of nonedible fats and fatty oils for the oxidation of pigments to colorless forms (see FOOD PROCESSING).

11. General Consideration for Application of Enzymes

There are two applications of the biocatalysts in textile bleaching operations, ie, bleaching of the textile material itself and treating the bleaching effluents. For substrate in solution, the enzymes may be applied either in free or immobilized form.

Production of high quality textile materials should be carried out through processes that are low in bath volume, reagents dosage, as well as short in processing time. The feasibility of an enzymatic laboratory-scale process for industrial application depends on the specific technology cycle adopted in the textile plant and on the available equipment. The guidelines to set the operating conditions for enzymes application can be obtaines from pH and temperature profiles of enzymes activity. For practical application of biocatalysts it is important to know the rate of acivity decay during process. The activity of enzmes is determined normally for soluble substrates in a homogenous catalysis reaction media, which differs significantly from textile-industry conditions (in the textile industry). In the textile industry, the substrate is insoluble and the wet processes are caried out at high turbulence and mechanical agitation in the textile baths.

Industrial implementation of new biotechnological processes and products in the bleaching stage of textiles not only will replace hazardous chemicals by biodegradable, naturally based products, but will also respond to the contemporary social needs by contributing to the quality of life, health, and safety of citizens of involved communities.

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