

# Bleaching of cellulose by hydrogen peroxide

**S. H. ZERONIAN\* AND M. K. INGLESBY**

Division of Textiles and Clothing, University of California, Davis, California 95616, USA

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Peroxides are important bleaching agents, industrially, for cellulosic products. They are also used in detergents. Peroxides can degrade cellulose as well as decolorize it and remove stains. Both free radicals and perhydroxyl anions have been suggested as the intermediates in the reactions occurring between cellulosic products and hydrogen peroxide. The proposed mechanisms are reviewed with emphasis primarily on cotton cellulose. Further work is required to establish unequivocally the mechanism of degradation and decolorization of cellulose products.

KEYWORDS: Hydrogen peroxide; oxycellulose; bleaching; oxidation

## INTRODUCTION

Peroxides are important bleaching reagents for cellulosic products. It has been reported that in 1993, for North America, the consumption of hydrogen peroxide by the pulp and paper industry was 530 million pounds and 60 million pounds by the textiles industry (Reisch, 1995). Hydrogen peroxide and related peroxy compounds are the most widely used textile bleaching agents especially in the United States (Vigo, 1994). Pulp bleaching is accomplished in successive stages each of which is characterized by appropriate chemicals and conditions (Sjöström, 1981). The chemicals used include  $\text{ClO}_2$ ,  $\text{Cl}_2$  and  $\text{NaOCl}$ . Hydrogen peroxide is used to reduce or eliminate such reagents (Reisch, 1995; Johnson, 1994). Peroxygen bleaches, predominantly perborates, can be incorporated in detergents and hold about 13% of the US detergent market (Ainsworth, 1995).

While peroxides are used to eliminate color or stains from textiles and to improve the brightness of pulps, it can also degrade the cellulose substrate. There have been many reviews of the technology of peroxide bleaching, including some discussion of the mechanism of the reactions that take place (for example, Valko, 1955; Peters, 1967; Andrews, 1979; Lewin, 1984; and Vigo, 1994).

The objective of this review is to discuss the reactions of peroxide bleaches, the catalytic effects of heavy metal ions, the functions of various auxiliaries and the reaction products. The emphasis is primarily on cotton cellulose. However the same principles also apply to lignocellulosics.

\*To whom correspondence should be addressed. Fax (916) 752-7584.

## PEROXIDE BLEACHING

Bleaching occurs when colored matter is either solubilized and removed or the unsaturated or conjugated chromophoric sites are altered or destroyed. It is well known that hydrogen peroxide solutions generally react quite slowly at low temperatures and pHs (Valko, 1955). Although the dissociation of hydrogen peroxide, as shown in equation (1), increases with rising temperature, the concentration of the perhydroxyl ions depends to a much larger extent on the pH of the solution (Andrews, 1979). The dissociation of hydrogen peroxide occurs at a pH of about 10–12 because it is a very weak acid ( $K_{\text{diss}} = 1.78 \times 10^{-12}$  at 20 °C). The formation of perhydroxyl anion has been widely described as important for the bleaching reaction.

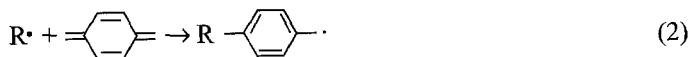


In practice textile bleaching is performed at high temperatures under alkaline conditions using NaOH and  $\text{Na}_2\text{CO}_3$  together with stabilizers and wetting agents. Stabilizers are added to minimize the decomposition of hydrogen peroxide and the perhydroxyl ion by forming complexes with heavy metal cations (see below). The most important types of stabilizers are sodium silicate and phosphonic acids (Weck, 1989). Prevalent phosphonic acids are aminotri(methylenephosphonic acid), ethylenediaminetetra(methylenephosphonic acid) and diethylenetriaminepenta(methylenephosphonic acid) (Rösch, 1988).

An extensive discussion of different types of stabilizers has been given by Lewin (1984). Stabilizers are thought to act partly by a buffering action to prevent the pH increasing too high. In the case of silicate stabilization, it is also thought to occur by either the formation of a complex with the hydrogen peroxide to prevent interaction with metal ion catalysts (see below) or by forming a colloidal suspension that absorbs metal catalysts, especially in the presence of calcium and magnesium ions. Phosphonates act by sequestering metal ion catalysts.

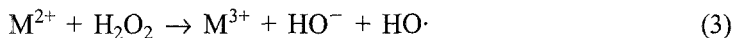
A free radical mechanism and a nucleophilic attack by perhydroxyl anions have been proposed for the reaction with chromophore groups.

The formation of free radicals from hydrogen peroxide requires the transfer of an electron from a donor to the peroxide. It has been suggested  $\text{HO}\cdot$  or  $\text{HO}_2\cdot$  demobilize the mobile electrons present in the systems of conjugated double bonds present in chromophores and thus decolorize the compounds (Taher and Cates, 1975; Steinmiller and Cates, 1976). For example a quinoid chromophore can be converted to a benzenoid structure (equation (2)).

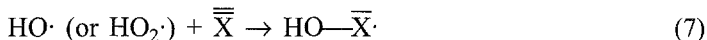
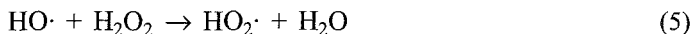
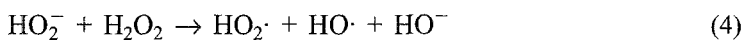


To demonstrate the effectiveness of free radicals as bleaching agents for cellulosic products, Taher and Cates (1975) studied the effect of the  $\text{H}_2\text{O}_2$ -HBr system. Such a system would not be utilized for bleaching cellulose material due to the acidity of HBr. However in the presence of HBr the bleaching activity and rate of peroxide decomposition is appreciably greater than in other acid peroxide systems. They stated that this was due probably to the ability of HBr to initiate decomposition of the peroxide to form hydroxyl and bromine radicals.

The proposed sequence of reactions in alkaline solutions of the hydrogen peroxide was as follows:



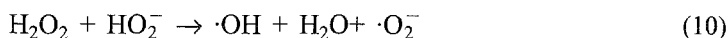
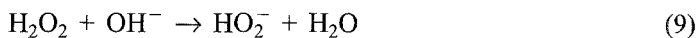
or following the reaction of equation 1



where M,  $\bar{X}$  and  $\bar{X}$  represent a metal ion, chromophore, and oxidized chromophore, respectively.

Decomposition of the hydrogen peroxide when no fabric was present was thought to occur by equations (3), (5) and (6). Initiation occurred due to metal ions present in the reaction vessel by equation (3). The molecular oxygen produced by equation (6) was said to be harmful to the cellulose in the alkaline medium. Equation (7) represented the bleaching. Convincing evidence that the production of free radicals by equation (4) was said to be lacking.

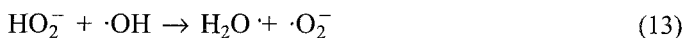
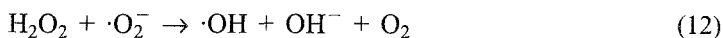
Isbell and coworkers (1981) have presented the following reactions for hydrogen peroxide in an alkaline medium.



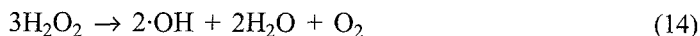
Followed by



Alternatively decomposition takes place by a chain reaction utilizing equations 12, 13 and 9.



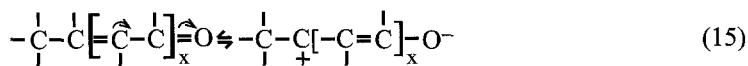
Isbell and coworkers found that the contribution of the chain reaction to the decomposition of the hydrogen peroxide increased as the temperature was raised. The chain can be initiated by traces of a catalyst and can be terminated, for example, by equation (11). The sum of the reactions given by equations (9), (10) and (12) gives



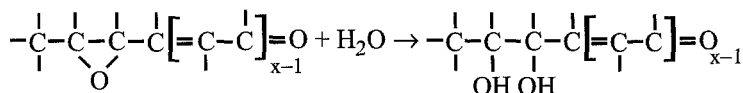
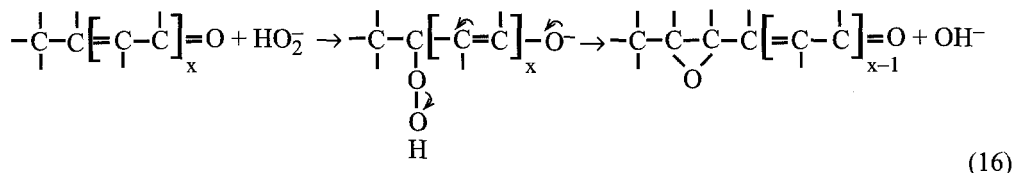
Thus Isbell and coworkers state that the decomposition of hydrogen peroxide by the hydroperoxide anion provides an abundant source of one of the strongest oxidants known, namely the hydroxyl radical. More recently Dannacher and Schlenker (1990) have proposed that bleaching is caused by the radical anion  $\cdot O_2^-$  rather than the hydroxyl or perhydroxyl radical. Complete details of the experimental basis on which their hypothesis is based are not given in their paper.

It has been proposed that the perhydroxyl anion, as a nucleophile, might attack carbon-carbon double bonds present in the chromophores of impurities. The mechanism

has been extensively discussed (Ney, 1982). Ney proposes that polarization of conjugated double bonds occurs.



Also the perhydroxyl anion attacks preferably at the end carbonyl atom. Thus:



Electrophilic attack at the carbonyl oxygen is also thought to be feasible.

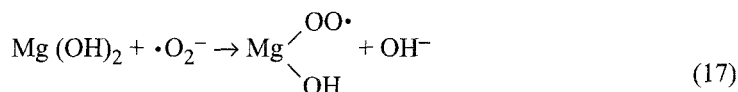
Ney states that the formation of hydrogen peroxide free radicals needs to be prevented since, in addition to reacting with colored compounds, they can attack and degrade the cellulose substrate. Impurities in the bleach solution would initiate the formation of hydrogen peroxide free radicals. For example, rust in the water would provide ferric ion which could react with the hydrogen peroxide. Thus he believes that besides controlling the perhydroxyl ion, stabilizers are required to prevent the formation of hydrogen peroxide radicals.

In the case of raw cotton, the color is due to pigments, namely a variety of high-molecular-weight compounds such as aromatic quinones or heterocyclic pyrrole derivatives together with auxochromic groups (Ney, 1982). In the case of lignocellulosic material the color is primarily due to the lignin. Gierer and Imsgard (1977) have concluded that alkaline hydrogen peroxide, due to the presence of hydroperoxide anions, will remove the original chromophoric structures in the initial phase of the reaction. This is due to the addition of the hydroperoxide anions to carbonyl groups and conjugated carbonyl structures. Later, as part of the hydrogen peroxide decomposes to yield oxygen and such reactive oxidation species as hydroxy and hydroperoxy radicals and singlet oxygen, secondary oxidations may occur resulting in lignin degradation, i.e. fragmentation and/or formation of quinoid, and other conjugated intermediates causing discoloration.

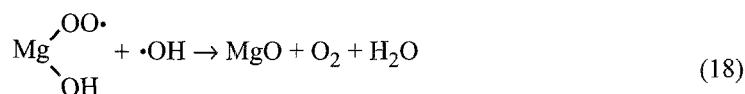
## ROLE OF METALS

Iron(II), Co(II) and Mn(II) are very effective catalysts for the homolytic decomposition of hydrogen peroxide in low concentration although they can retard oxidation at high concentrations (Gilbert, 1973). Such metals may occur as impurities in the bleaching solution. There are several sources for such metals. They may be inherent impurities in the raw cotton. Other possibilities are: metal particles transferred from the spinning and weaving machinery; metal-containing soil deposited on the yarn, if the open end spinning process is used; in some cases metals may be present in the bleaching chemicals (such as iron in the sodium hydroxide and in the sodium silicate); finally, there may be rust in the pipes (Reicher, 1992).

Magnesium compounds retard cellulose oxidation that is catalysed by transition metals. Nevell (1985) has discussed possible explanations for the retardation. One is the formation of stable complexes between the transition metal, magnesium and an aldonic acid which has either been formed by oxidation or added with the magnesium. Another is that the magnesium ions complex with some of the intermediate products of the degradation. Isbell and coworkers (1981) assume as a working hypothesis that the superoxide radical forms a complex with the magnesium compound (equation (17)). This complex would immobilize and possibly precipitate the superoxide radical.



Its removal by any means would inhibit production of the hydroxyl radical and thus lessen the oxidative capacity of the reaction mixture. They also state the complex may also act as a scavenger for hydroxyl radicals (equation (18)).



Their hypothesis does not explain why magnesium hydroxide is much more effective than other hydroxides.

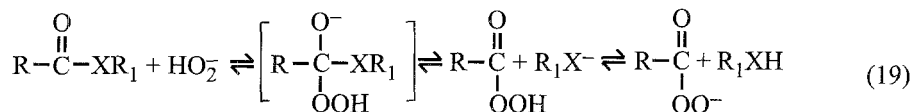
In a study by Reicher (1992) it was demonstrated that the iron content of selected raw cotton fabrics varied from 34 to 790 mg kg<sup>-1</sup>. It was also shown that metal-catalysed local decomposition of cellulose, resulting in the formation of holes, could be simulated by using bronze powder and with copper applied electrochemically to iron filings.

Another source of metals are metal complex dyes. Fabrics dyed with such products are degraded and discolored during bleaching unless a chelating agent is present (Imabayashi, 1995).

## PEROXIDE CATALYSTS

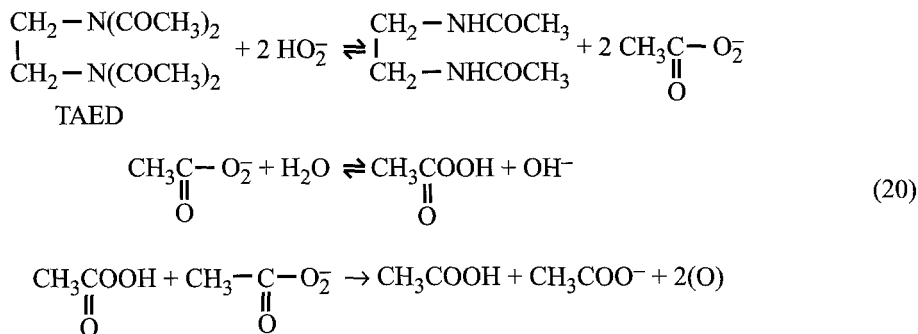
Perborates, which are solids and liberate hydrogen peroxide in solution, are the predominant bleaching component in household detergents (Ainsworth, 1995). The wash water temperature in the US is normally lower than in Europe. In the US, perborate tetrahydrate has been displaced by perborate monohydrate which is more soluble under US laundry conditions (Ainsworth, 1995). The traditional European powdered detergent contains sodium peroxoborate or sodium carbonate peroxohydrate. To maintain acceptable bleaching activity at washing temperatures down to 40 °C tetra-acetylenediamine (TAED) can be added (Freemantle, 1994).

Becker (1976) has discussed a number of different activators which are N- or O-acetyl compounds including TAED. He states that the perhydroxyl anion formed in a perborate solution will react with the activator to form a peracid as follows.



where X = O, NR<sub>2</sub>, etc.

Kleber (1994) discussed the bleaching mechanism as due to the formation of active oxygen in the following manner.



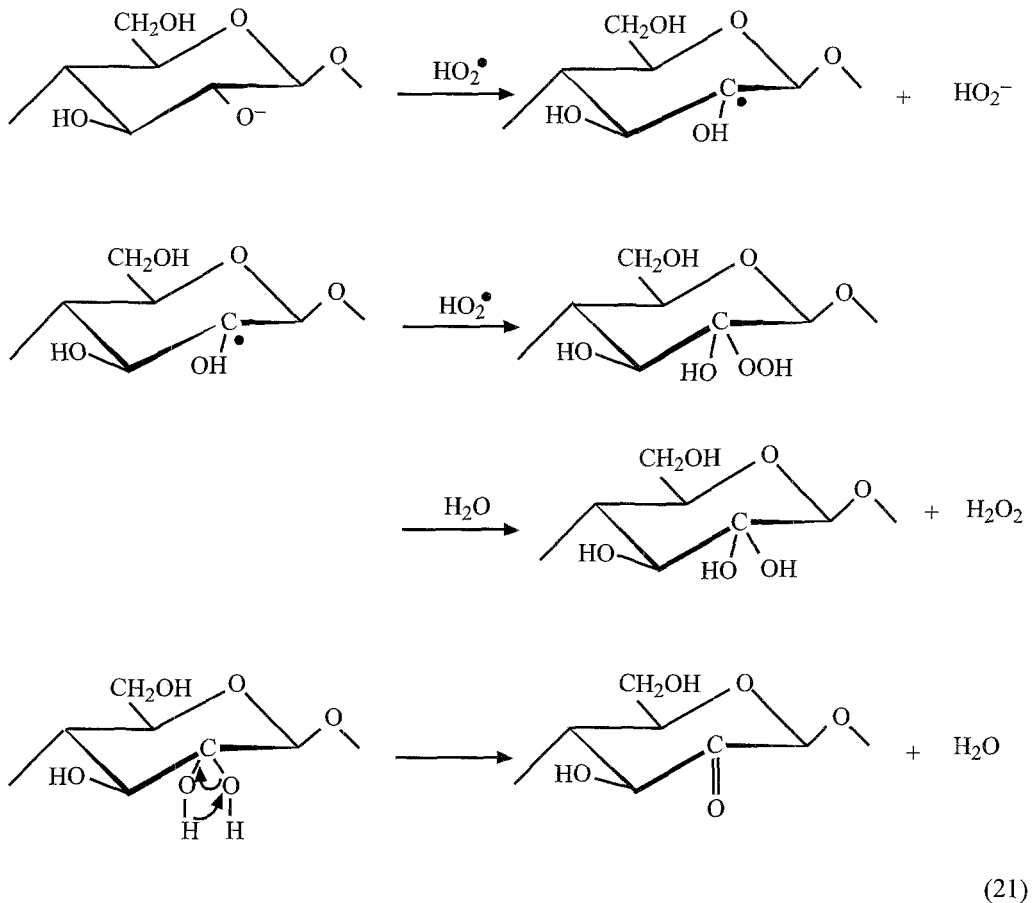
TAED is used in Europe but not in the US where one activator that has been commercialized is nonanoyloxybenzene sulfonate (NOBS), which is incorporated in several detergent products (Farr *et al.*, 1992). NOBS is used also in Japan. It produces pernonanoic acid when combined with hydrogen peroxide.

Organomanganese complexes derived from either 1,4,7-trimethyl-1,4,7-triazacyclononane or substituted triazacyclononane ligands have been reported recently as highly effective catalysts for the bleaching of stains by hydrogen peroxide at low temperatures (Hage, 1994). The active oxidizing species is unknown. Mixed-valence Mn(III)/Mn(IV) compounds might be involved. The question has been raised whether these catalysts cause fabric damage under certain working conditions (Verrall, 1994).

## OXIDATION OF CELLULOSE BY HYDROGEN PEROXIDE

The degree of polymerization of cellulose can be lowered by the reaction with hydrogen peroxide and it can be transformed into an oxycellulose. Lewin and Ettinger (1969) made a comprehensive study of the reaction between hydrogen peroxide and cellulose in the form of purified cotton fibers. They differentiated between the hydrogen peroxide that decomposed and the hydrogen peroxide that oxidized the cellulose. The purified cotton contained a small amount of iron. If the iron was extracted from the purified cotton with 0.1 M HCl, decomposition was relatively strong and oxidation was relatively slow. Thus they suggested that the  $\text{HO}_2^-$  ion is, by itself, not highly effective in oxidation and suggested that the traces of iron normally found in cotton bring about a marked catalytic effect possibly by the formation of active complexes between iron and the  $\text{HO}_2^-$  ion. In an experiment conducted at a pH of 9.5–9.7 and a temperature of 80 °C Lewin and Ettinger found that as the oxygen consumption increased the carboxyl content increased progressively to 0.63 meq per 100 g, aldehyde to 0.19 meq per 100 g and ketone to 8.92 meq per 100 g (values after the deduction of the value of the nonoxidized control). Thus the oxidation predominantly formed ketone groups and they hypothesized that these functional groups occurred primarily at C<sub>3</sub>. During the oxidation the degree of polymerization decreased markedly as well. They stated the ketones were 'inactive' carbonyls. That is, they did not cause a splitting off reaction and consequently there was almost no yellowing of the cotton during ageing or hot alkaline extraction.

Ney (1982) suggests in an alkaline solution it is the perhydroxyl radical that oxidizes cellulose in the following manner at both the C<sub>2</sub> and C<sub>3</sub> carbon atoms.



Following the formation of the keto groups Ney hypothesizes several different reactions can occur. However, no experimental evidence is provided.

Meyer *et al.* (1987) have proposed that the damage to the cellulose by the presence of metal particles, adhering to yarn and fabric during bleaching, is caused in two ways. First, by catalysing the generation of free radicals. Secondly, by decreasing the pH of the solution and causing acid hydrolysis. The reduction in pH is stated to be caused by the hydrolysis of metal ions (pH 1–2 in the case of iron).

## CONCLUSION

Progress has been made in establishing the reactions that can occur when peroxides are used as bleaching agents. However there is still no general agreement on the species which is primarily responsible for the bleaching action and for the degradation of the cellulose itself. Thus definitive research remains to be done.

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