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Peroxide Bleaching

Peroxide bleaching has made significant strides during last two decades. Today, nearly half of the bleached groundwood pulp is produced by peroxide bleaching. It gives high degree of brightness at low cost with little or no loss of yield and with less tendency for colour reversion in bleached pulp. In the bleaching of chemical pulps it is generally used as last stage or intermediate stage in order to achieve significant brightness gains witout appreciable loss of strength. This article reviews available literature on peroxide bleaching. Process conditions for bleaching different type of pulps have been discussed and typical recipes have been suggested for certain types of pulps.

INTRODUCTION

The colour of unbleached pulp varies from light brown to dark brown depending upon the process of pulping. The main constituents of pulp, cellulose and hemicllulose, are essentially white in colour. Even the lignin is considered colourless or light in colour. Therefore it seems that the dark colour of unbleached pulp mainly comes from the chemi cal changes taking place during pulping. Some derivatives of lignin, specially the chormophoric and auxochromic complexes from the phenolic groups of the lignin molecule, are considered to be mainly responsible for the dark shades of unbleached pulp. The resin content of original wood may also be responsible to some extent for the colour of unbleached pulp.

The main object of bleaching is to remove or alter the colour bearing complexes. A large number of chemi. cals are used for achieving this object, viz. chlorine and chlorine com. pounds, sulphur dioxide, bisulphites, dithionites and peroxides. Some of these agents are destructive in the sense they remove colouring compounds and reduce the yield, whereas there are others which improve the colour of pulp with little or no decrease in the yield of pulp. The chlorine and hypochlorites improve colour by removal of the colour bearing complexes and therefore are destructive whereas chlorine dioxide, peroxide and dithionites etc. can improve the colour of pulp without removing the complexes. Chlorine dioxide is generally used for bleaching the chemical pulps while peroxides and sulphur compounds are extensively used for bleaching ground wood and other high yield pulps.

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2. Mechanism of Peroxide bleaching:

The bleaching action of peroxides is entirely different from that of other oxidative agents. In case of other oxidants, the colour bearing noncellulosic compounds are attached and rendered soluble, to be removed in subsequent stages by extraction. This results in loss of yield and to some extent in the loss of strength and other propeties of pulp. However, in peroxide bleaching, the colouring constituents of colour bearing compounds are rendered inactive without significant alteration in the main structure of colour bearing compounds. This is achieved at comparatively low cost and therefore peroxides are used for bleaching of mechanical and high yield pulps where final yield is of great importance. They are also used in the final stages of chemical pulp bleaching where brightness can be increased by a few points with little chemical consumption.

2.1 Ionisation of hydrogen peroxide:

Hydrogen peroxide ionises as,

$$H_2O_2 \rightleftharpoons H^+ + OOH^-$$

Because of the presence of H^+, the aqueous solutions of pure hydrogen peroxide are weakly acidic. It is generally believed that the perhydroxyl ion (OOH^-) is the active bleaching agent. The dissociation constant of hydrogen peroxide at room temperature is 2×10^{-12} but increases with temperature and is nearly 10 times (2×10^{-11}) at 80°C. Though the increase in temperature is accompanied by corresponding increase in dissociation constant, beyond certain limits, the increase in temperature, increases the reactivities of alkali with the pulp, resulting in what is called "browning action". Therefore it is desirable to have the proper balance of pH and temperature so as to achieve a maximum brightness with minimum amount of chemical consumption.

Increase in pH value, favours the dissociation of peroxide. The addition of alkali results in reduction of hydrogen ions and in corresponding increase of perhydroxyl ion. However there is upper pH limit imposed by following non reversible reaction.

$$2OOH^- \rightarrow O_2 + 2OH^-$$

The upper limit for pH is found to be in the vicinity of 11.5, because if pH is below 9, there is limited dissociation of peroxide and practically there is no bleaching action. Therefore it is essential to maintain a narrow range of pH (between 9 to 11.5) during peroxide bleaching.

2.2 Decomposition of Hydrogen peroxide:

Hydrogen peroxide decomposes according to following equation,

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The presence of certain metallic ions like cupric, ferric, and also of manganese and nickel readily catalyses the decomposition of hydrogen peroxide. To minimise the decomposition, it is necessary to immobilise the metallic ions. This can be easily achieved by addition of magnesium sulphate and sodium silicate to the bleaching solution. If the metallic ions are present in significant quantities then the application of special chelating agents like diethylene-triamine penta-acetic-acid, may also be considered. Sodium silicate in the bleaching solution plays the important role of a buffering agent as well. During bleaching action some carboxylates and phenolates are formed which are stronger acids than perhydroxyl ions. This results in the drop of pH and significant caustic consumption in the initial stages of bleaching. Sodium silicate buffers this reaction through the bleaching process by liberation of the hydroxyl ions at the desired rate. However too high a silicate concentration may retard the bleaching reaction.

3. Variables in Peroxide Bleaching :

The important variables in bleaching of pulps by peroxides are the temperature, consistency, peroxide concentration, initial alkalinity, time, residual chemical, wood, species and pulp quality. All these variables affect the efficiency of bleaching reaction. These variables also have a tendency to interfere with one another and therefore the optimum conditions for a particular case must be decided upon, after trying different combinations of variables experimentally. The effect of different variables individually is discussed below.

3.1 Effect of proportion:

An increase in the quantity of peroxides added per ton of O. D. pulp increases the brightness initially but curves flatten out soon, as shown in Fig, 1.

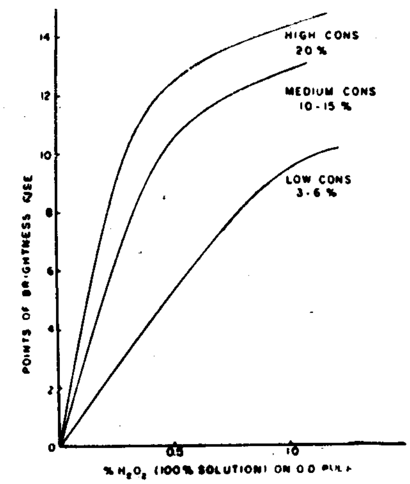

Fig. 1. Effect of pulp consistency and peroxide application on bleached brightness.

3.2 Temperature :

Increase in temperature increases the rates of bleaching reactions and reversion reactions simultaneously and therefore it is necessary to adjust the temperature level carefully for the best possible results. In order to choose a suitable temperature, the effect of alkalinity must be also considered. In practice it is found that maximum brightness is obtained in the range of 40–60°C. Lower temperatures tend to extend the bleaching time while high temperatures lead to colour reversion. In general the bleaching time increases about two fold for every 10°C drop in temperature. In the bleaching of chemical pulps the temperatures are kept slightly higher. Fenell[2] *et al.* report the development of a high temperature groundwood bleaching process by Du Pont. A reaction time of 10 min, at 90–95°C was tried with spruce ground wood and the results obtained were comparable to the results in normal bleaching for one to two hours at low temperatures. Fig. 2 compares the conventional and high temperature bleaching of ground wood pulps.

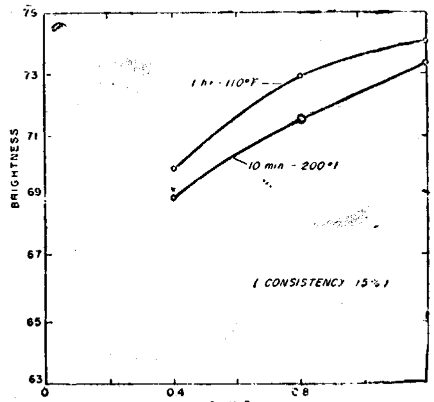

Fig. 2. Conventional vs. high temperature peroxide bleach on groundwood; effect of peroxide[2]

3.3 Alkalinity:

The rate of both the bleaching and reversion reactions increases with the increasing pH. For maximum brightness and minimum bleaching time, the system should have an initial pH of approximately 10.5. This pH is generally provided by a total alkali level (as NaOH) of 1 to 3 % based on O. D. weight of the pulp, depending on the peroxide concentration used. The exact level of total alkali is also determined by the consistency of pulp, process temperature and bleaching time. Higher alkali is preferred for bleaching at low pulp consistency and low temperatures, whereas lower alkali valve is desirable for bleaching at higher consistencies and temperatures. Ferguson[3] *et al.* studied the effect of alkali on brightness and the results are shown in Fig 3.

They have plotted the brightness against the time for three different levels of peroxide concentration,

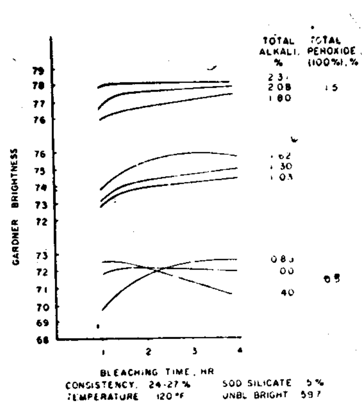

Fig. 3. Effcet of total alkali on brightness rise.

with varying amounts of alkali. The temperature in all the experiments was 49° C.

3.4 Time :

The rate of peroxide consumption depends on temperature, consistency and alkalinity of reactions. Usually the peroxide is consumed more rapidly during initial bleaching period and then the rate of consumption progressively falls down.

3.5 Pulp Consistency :

Higher the pulp consistency, better is the degree of brightness obtained with a given amount of peroxide. The bleaching time also reduces with increase in consistency. Maximum brightness can be obtained in 4 hours at 25% pulp consistency compared to 10 hours at 3% consistency. Figure 4 gives an interrelation of

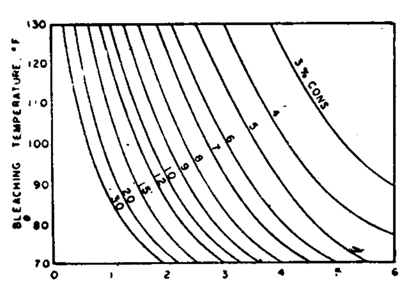

Fig. 4. Effect of temperature and consistency on bleaching time

time, temperature and consistency in bleaching.

3.6 Stabilizers :

Sodium silicate and magnesium sulphate are used as stabilizers to control the rate of decomposition of peroxide bleach liquor. The stabilizers should be free from heavy metal impurities. The amount, of silicate used depends on the total alkalinity of the bleach liquor and the quantity to be used is calculated to give Na_2O : SiO_2 ratio as approximately 1.25 : 1.00. The amount of $MgSO_4$ required would be 1/4 Kg. per cubic meter of bleach liquor.

3.7 Residual Chemical:

It is desirable that some minimum amount of peroxide be present, after the bleaching reaction is complete. According to Martin[5], this minimum residual peroxide is required to bleach the products of reversion reaction which continues until the residual alkali is completely consumed. The optimum level of residual peroxide varies between 10-20% for mechanical pulps,and the level of residual alkali should be lower than this to avoid reversion reaction.

3.8 Wood species and pulp quality:

Peroxide bleaching with different wood species has been investigated and reported by many 6,7,8,9. It has been found that some varieties respond readily to peroxide treatment but some others are not easily bleached probably because of the presence of some extractives,

Storage of pulp affects its bleachability by peroxides because of certain bacterial growth. Refiner ground wood pulp contain metallic ions and treatment of such pulps with chelating agents is necessary in order to take care of metallic ions.

4. Ground wood Pulps:

The bleaching of ground wood pulps by peroxides started on commercial scale in U.S.A. in 1941. Today more than 50% of groundwood bleached pulp is produced by peroxides bleaching although the nature of reactions in bleaching of groundwood pulps by peroxides is not yet fully established.

Peroxide bleaching does not alter the properties of pulp significantly. As reported by Beeman[10] *et al* the bulk, strength properties and freeness remain unchanged in peroxide bleaching. Opacity also is only slightly lowered. Rhodes[11] has reported that the printing properties of groundwood paper are improved by use of peroxide bleached ground wood pulps.

Witkowski[12] has mentioned three techniques in single stage bleaching viz. at 9-12% consistencies, at 30 percent or higher consistencies and by spraying the solution of peroxide on the sheeted pulp if the pulp is to be marketed in the form of pulp sheets. He has also mentioned two stage peroxide-hydrosulphite bleaching and considers it to be more economic for brightness gains of 13-20 points. The order of bleaching consists of a peroxide stage followed by a hydrosulphite stage with a sulphur dioxide treatment in between the stages to reduce the residual peroxide.

4.1 Process Details:

The bleaching is carried out in a single stage by treating freshly groundwood pulp with hydrogen peroxide under controlled conditions of temperature, alkalinity and consistency.

A typical recipe given below with slight variations to suit site conditions, will produce maximum brightness and good yield, with high or medium density pulps.

Epsom salt ($MgSO_4 . 7H_2O$)	-0.025 %
Sodium Silicate, 78°Tw (SiO_2 29%, Na_2O 8.8%)	-3-5.00%
Caustic Soda	-0.6-6.8%
Hydrogen peroxide 35%	-2.5-3.00 %
or	
Hydrogen peroxide 50%	-2.0-2.25%
Retention time	-3-5 Hrs.
Temperature	-40-60°C.
(% on O. D. weight of pulp)	

The bleach liquor is mixed with the pulp previously thickened and heated under controlled conditions. The retention time is suitably adjusted to effect complete bleaching.

After the peroxide bleach, the pulp is washed and neutralized/reduced by treatment with 0.3-1 0% sulphur dioxide (on the weight of O.D. pulp) with a retention time of 30-45 minutes at ambient temperature followed by washing.

5. Cold Soda Pulps:

Single stage bleaching of cold Soda pulps is widely practised in industry. Cold soda pulps can be bleached in refiners for moderate brightness gains of 55-65 GE. Tower bleaching can be used for higher brightness gains up to 65-75 GE. The bleachability of cold soda pulps varies with the wood species and age and therefore laboratory scale bleaching investigations are essential for planning the mill scale bleaching processes. A typical process for peroxide bleaching in the refiner is shown in fig. 5. The dosage of chemicals include 5% Sodium Silicate, 0.6-1.5% hydrogen peroxide, 0.4-0.6% sulphuric acid. The pulp is bleached for about 15 min. at about 75°C. and then neutralized with SO_2 to a pH value of 6.

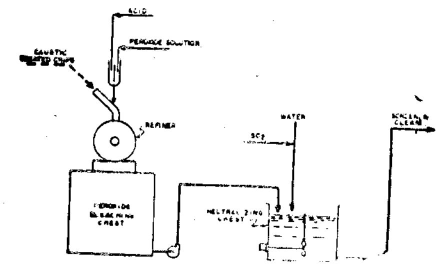

Fig 5. Typical process for peroxide bleaching in the refiner

6. NSSC Pulps:

NSSC pulps can be bleached to about 85 GE brightness with CEH sequence with washiug in between the two stages. But the chemical requirements are very high and loss in yield may be as much as 20% of unbleached pulp, because of the large amount of lignin removed. Single stage peroxide bleaching can give satisfactory brightness levels with very little loss in the yield, and these bleached pulps can be easily used for ordinary writing and printing grade papers. In peroxide bleaching the shrinkage is less than 3% and compared to about 15-20% in CEH sequence. About 2-3% Na_2O is required preferably at high consistency, high temperature (greater than 50°C) and for extended time.[14]

7. Chemical Pulps:

Use of peroxides for bleaching kraft pulps started in U. S. A. in early fifties. The main aim was to obtain increased brightness with no significant loss of strength, or to obtain good brightness stability. In India, most of the mills produce kraft pulp from bamboo or wood and the typical bleaching sequences used in the industry are CEH, CEHH or CEHEH. If peroxide stage is included as a final stage, replacing hypochlorite stage, a brightness level better than conventional sequence with very little colour reversion is obtained.

Unbleashed kraft pulps are not readily reacted upon, by peroxides and for minor brightness gains reductive bleaching with dithionites gives better results. Probably the most economic proposition for higher brightness gains, would be to bleach with chlorine and hypochlorites to about 2–4 brightness points below the desired final value and then give the finishing touches with peroxide stage. For brightness levels in the vicinity of 90 GE, inclusion of a chlorine dioxide stage is imperative.

Unbleached sulphite pulps can be easily bleached to 75 GE brightness[15] by peroxides only. In bleaching of sulphite pulps, peroxide stage is also used in extraction or finishing stage, depending on the conditions of the mill. The temperature range for bleaching kraft pulps is slightly higher (75–85°C) compared with sulphite pulps 40–60°C).

7.1 Process Details:

The amount of peroxide needed for chemical pulps is less than that required for high yield pulp. The exact concentration etc would depend upon the pulp and process adopted. A typical recipe and process conditions are given below.

Epsom Salt ($MgSO_4 \cdot 7H_2O$)	0.025%
Sodium Silicate, 78°Tw	2.5%
Caustic Soda.	0.4–0 6%
Soda Ash.	0.6–0.75%
Hydrogen peroxide 35%	1–1.5%
Or	
Hydrogen peroxide 50%	0.75–1.0%
Consistency.	10–15.1%
Time.	3–5 Hrs.
Temperature.	60–80°C.

Although stabilisation with magnesium Sulphate and Sodium silicate is most effective but almost equivalent results have been obtained with a combination of magnesium sulphate, gluconic acid and alkaline buffers[16]. The treatment of chemicals pulps resembles that of the ground wood pulp described earlier.

Preparation of Bleach Liquor.

The bleaching solution can be prepared either batch wise or in a continuous automatic system. In the batch system, cold water is first added to the tank and the agitator started. Requisite quantity of epsom salt followed by sodium silitate, caustic soda and finally hydrogen peroxide are added and mixed well.

The continuous system consists of a cascade type stainless steel mixing tank. Water and epsom salts are metered to the first compartment, sodium silicate to the second and hydrogen peroxide to the third compartment of mixing tank. Caustic soda or soda ash may be added to second compartment for the control of alkalinity. By gravity, then liquor flows from third compartment to a bleach liquor storage tank.

9. Chemical used in Peroxide Bleaching.

9.1 Hydrogen peroxide.

It is a versatile industrial chemical used in textile, pharmaceutical, chemicals, paper and range of other industries. The concentrations supplied to industry in India are 35% and 50% by weight (W/w). Some of the physical properties are given in table 1.

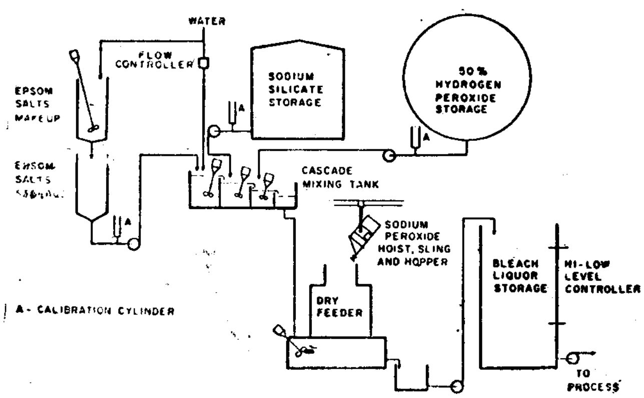

Fig. 6. Continuous peroxide bleach liquor makeup.[13]

Table 1. Physical properties of hydrogen peroxide.

Physical property.	35% H_2O_2	50% H_2O_2
1. Approx. vol. strength.	131	197
2. Active Oxygen %W/w.	61.5	23.5
3. Density at 20°C, gm/cc	1.131	1.195
4. B. Pt. (at 760 mm Hg)°C.	108	114
5. Freezing point °C.	–33	-51
6. Refractive Index ($_nD25$)	1.355	1.366

Hydrogen peroxides is a clear, colourless, odourless liquid with oxidising propoıties. It is miscible with water in all proportions and insoluble in hydrocarbons. Commercially packed hydrogen peroxide is highly stable at normal temperatures because of high degree of purity and stabilizing additives. It is packed in containers made out of glass, specially treated high purity aluminium or in low or high density polyethylene. It should be stored in original container in a cool place away from sources of heat.

9.2 Sodium Peroxide

It is a pale yellow, granular solid containing a minimum of 96% Na_2O_2 and 19.6% active oxygen. It is stable at ordinary temperatures when kept dry in air tight containers. It can be dissolved in water without significant loss of active oxygen if proper technique is used. It can cause combustion of organic material by heat or friction or with small amount of water. One kg. of sodium peroxide is equivalent to 1.19 Kg of 35% H_2O_2 or 0.84 kg of 50% H_2O_2. As Sodium peroxide is a strong alkali it cannot be used alone. It should be used either with hydrogen peroxide in proper proportions or sulphuric acid must be used for maintaining proper alkalinity.

9.3 Sodium Silicate

It is available as solid (silicate glass) or in the form of solution. Special equipment is needed for dissolving it, if purchased in solid form. It should be free from metallic impurities. It has the property of a detergent and penetrant and it buffers the bleaching solution. It stabilizes the peroxide solutions under the conditions prevalent in pulp bleaching. It also inhibits corrosion of metal by forming a protective layor on the metallic surface.

9.4 Epsom Salt

It inhibits the effect of metallic ions and stabilizes the peroxide solutions. This action is due to the formation of magnesium silicate.

9.5 Caustic Soda

It is most economical chemical available for controlling the pH of the solution. Use of sodium silicate may be made in place of caustic soda but sodium silicate is quite costly.

9.6 Neutralizing agents.

Sulphur dioxide is most commonly used for neutralizing the pulp slurry after bleaching. In some instances sodium bisulphite and sulphuric acid may also be used for lowering the pH to desired level. It destroys the remaining alkali, reduces coloured ferric ion to colourless ferrous ion and destroys the traces of peroxides remaining in pulp.

10. Material of Construction.

Peroxide bleaching should be carried out in equipment of stainless steel, alkali resistant tile or cement concrete. Copper, brass or lead equipment should not be used as they may cause catalytic decomposition of hydrogen peroxide bleach liquor. Storage tanks and piping should be of high purity aluminium while pumps may be of stainless steel type 304, Packing material should be Teflon or Teflon asbestos lubricated with a silicone. Gaskets should be of polyethylene or Koroseal[13]. Dilute alkaline solutions require stainless steel type 304, polyethylene or pyrex glass. Magnesium sulphate should be dssolved, stored and handled in stainless steel equipment while sodium silicate may be handled with steel pumps and stored in steel tanks.

References

1. FMC Corp. BECCO Chemical Div, 161 East 42 st. New York, Bulletin 117.
2. Fennel *et al Tappi* 43 (11) 903 Nov. 1960.
3. Ferguson D. M. *et al Pulp Paper Mag. Canada* 63 (4) : I—228–T 236 (1962).
4. Klemm K. H., "Modern methods of Mechanical pulp manufacture" Lock wood Trade Jounal G. Inc. New York, 1958.
5. Martin D. M. *Tappi* 40 (2) 65–75, Feb. 1957.
6. Kingsbury R. M., *et al, Pulp Paper Mag. Canada* 50 (4) 98-102 (1949)
7. Andrews D. H. and Des Rosiers P., *Pulp Paper Mag. Canada* 67 (C) : T119 (1966).
8. Lewis H F., *Tappi* 39 (6) 24 A-40 A, 1956.
9. Reichert J. S. and Pete R. H. *Tappi* 32 (3) 97–107, (1949).
10. Beeman J. A. *et al paper Trade Journal* 118 (24) 33–36 (1944).
11. Rhodes K, *Paper Trade Journal,* 118 (14) : 23 (1944).
12. Witkowski C. J., *Paper Trade Journal,* May 29, 1972.
13. Armstrong A. D. "Bleaching mechanical pulp" in Pulp and Paper manufacture Vol. 1, Mc Graw–Hill Book Co. New York, 1969 pp 205.
14. Kraft F. "Bleaching of wood pulps" in Pulp and Paper manufacture Vol. 1. McGraw–Hill Book Co. New York 1969, pp 674.
15. *ibid* pp 660
16. *Tappi*, 42 (4) 313-316