Short Bleaching Sequence-Acid Peroxide Delignification Vs Alkaline Peroxide Extraction For Achieving High Brightness of Hardwood Pulp

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ABSTRACT

Delignification of the unbleached hardwood pulp with catalysed acidic hydrogen peroxide treatment followed by conventional CEHH sequence was capable of producing a brighter pulp. Introducing hydrogen peroxide in the alkaline extraction stage also produced a high bright pulp. Comparison of both the sequences offer a suitable and viable short sequence which can be very easily retrofitted in the existing conventional CEHH bleaching sequence. Oxidative reinforced extraction integrating hydrogen peroxide with conventional CEHH sequence appears to be the most attractive. This system gains a special significance in view of the fact that more and more stress is being given on economic viability and process flexibility for achieving high brightness.

KEY WORDS

Acidic hydrogen peroxide, sodium molybdate, alkaline hydrogen peroxide, high brightness, delignification, pulp quality.

INTRODUCTION

Tamil Nadu Newsprint and Papers Ltd. is a large integrated bagasse based plant. The mill operates a single line CEHH bleached Eucalyptus hardwood kraft pulp designed to produce 72 MT/day, and it uses the wood pulp as a supporting fibre component in its furnish. Recent research works on pulp bleaching focus on various processes particularly, for achieving very high brightness (90 % ISO). Product diversification, and pressure in the market have forced many mills to look for the most economical solutions to achieve high brightness pulps with acceptable strength and cleanliness using minimum number of bleaching stages. The traditional bleaching sequence (CEHH) of hardwood now being carried out in the plant enhances the brightness only to a level of 75-78 % ISO. Further enhancement in the brightness of hardwood pulp by conventional bleaching sequence will yield an impaired pulp.

The thirst for reaching very high brightness has increased enormously as never before in the paper industry, and that has not been fulfilled satisfactorily. Alternative approaches are continually developed to tackle the problem. This strong desire has made the researchers to go for unconventional (becoming more and more conventional) bleaching methods using various oxidizing agents such as chlorine dioxide, oxygen, hydrogen peroxide and ozone. These applications illustrate the effectiveness beyond the conventional improvements in brightness and strength characteristics of the product. These unconventional bleaching methods offer enormous scope for further thrilling improvement.

Mounteer et al (1) achieved 90% ISO brightness in a short sequence using the combination of oxygen, ClO_2, and peroxide. Introducing an ozone stage to pulps pretreated with peroxy formic acids increased the brightness of both hardwood and softwood pulps to 90% ISO (2). Miller et al (3) described the oxygen delignification systems to achieve high brightness.

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Table-1		
Characteristics of the Unbleached Pulp		
1.	Brightness, %ISO	25.7
2.	Kappa number	21.8
3.	Viscosity, CP	12.3

Introduction of peroxide stage in the CEHDEP sequence gave pulp with 90% ISO brightness with improved pulp properties (4). Chlorine dioxide has been extensively used to bleach chemical pulp to very high brightness without significant loss of pulp strength (5). Displacement bleaching techniques using chlorine, chlorine dioxide and oxygen have been commercially exploited to achieve very high brightness (6). Lachenal et al (7) studied a new bleaching procedure (OXODED) where small amount of chlorine was included, to activate lignin, between two oxygen delignification stages to get very high brightness. Hence, development work is carried out to improve the brightness of our plant hardwood pulp to make such products compatible with all furnishes.

The objective of the present work is to develop a process for the economic utilization of hydrogen peroxide to determine if and to what extent acidic peroxide (AP) pretreatment and peroxide in E stage [E(P] can perform the oxidation, thus resulting in greater overall improvement in pulp characteristics. Although, there are few reports individually available on utilisation of peroxide in acidic and alkaline stages, this study is the first of this kind, which compares the efficiency of both the systems on the same pulp to produce high brightness pulp.

EXPERIMENTAL

Unbleached kraft screened hardwood pulp (Eucalyptus hybrid) was collected from our mill facility for bleaching experiments. Prior to the bleaching experiments the unbleached pulp was washed throughly to remove the residual alkali and the pulp consistency was increased to 30 % (w/w) in a hydro extractor. The characteristics of the unbleached pulp are given in the **Table-1.**

Acid peroxide delignification of the kraft unbleached pulp was carried out at 10% consistency in a thermostatic water bath at 85°C for 60 minutes. pH was maintained at 5.0 using 4N sulphuric acid, and 500 ppm sodium molybdate was added as catalyst. Peroxide was added to the pulp preadjusted to pH 5 and premixed with the sodium molybdate solution. This stage was performed in polythene bags using 50g (OD) pulp, while standard runs were carried out with 200g (OD) pulp. After the pretreatment, the pulp was subjected to CEHH bleaching sequence. The conditions maintained during different bleaching stages are given in **Table-2.**

The optimisation of chlorine in chlorination stage was carried out in plastic containers, using 20g (OD) pulp. Chlorine was applied as multiples of kappa number X 0.11, X 0.14, X 0.17, X 0.20, X 0.23%. The optimum chlorine dosage was determined by plotting chlorine(%) applied against residual chlorine. The corresponding chlorine dosage at the point of inflexion of the curve gave the optimum chlorine requirement. Standard runs were carried out in plastic containers with 200 g(OD) pulp using optimised chlorine dosage.

Optimisation of the extraction stage was carried out in polythene bags with different dosages of sodium hydroxide and the minimum dosage corresponding to a final pH of >10.5 was chosen as the optimum. Oxidative extraction using hydrogen peroxide as the

Table-2					
Optimised Bleaching Conditions for acid peroxide delignification and alkaline peroxide extraction					
Bleaching Stage	Charge %	Temp °C	CY %	pH	Time Min
Acid Peroxide (AP)	1.0	85	10	5.0	60
Chlorination after AP	2.1	Ambient	3	–	30
Chlorination before E(P)	3.1	Ambient	3	–	30
Caustic Extraction	2.0	60	8	>10.5	60
Hypo I as Cl_2	1.8	40	8	8.5 to 9.5	120
Hypo II as Cl_2 AP/EP	1.0/0.5	40	8	8.5 to 9.5	120

oxidant in the extraction stage was carried out by adding the required H_2O_2 on pulp along with the alkali, maintaining similar reaction conditions.

Calcium hypochlorite dosage was optimised so as to achieve 80% ISO final brightness in the conventional CEHH sequence. The hypo stage was carried out for 2 Hrs at 40°C in polythene bags in a thermostatic water bath, The pulps after each stage were washed with demineralised water equivalent to 20 times of the OD pulp taken.

ANALYSIS

Kappa number, viscosity, and strength properties were determined as prescribed in TAPPI standards. Brightness and scattering coefficient were measured using Elrepho brightness tester.

RESULTS AND DISCUSSION

DELIGNIFICATION WITH ACIDIC HYDROGEN PEROXIDE (AP)

The important variables which affect the rate of delignification are the H_2O_2 charge, temperature, catalyst and treatment time. The effect of these variables were examined in this study.

Influence of Hydrogen Peroxide Concentration

An optimization of acidic Peroxide stage was carried out on the unbleached pulp and the same was subjected to the different dosages of peroxide. The possibility of increasing the degree and selectivity of delignification with acidic peroxide pretreatment of the Kraft pulp was studied from the optimisation experiments. The results are shown in the **Fig.1.** The results reveal that 1% hydrogen peroxide on pulp is sufficient for optimum delignification. However increased dosages beyond 1% had no significant improvement on further delignification. One of the most important aspects of chemical pulp bleaching is the selectivity of the bleaching chemical. Selectivity can be defined as the relative reaction of the chemical with the lignin compared to cellulose. Peroxide is one of the highly selective chemical agent (8). The results show that on increasing the peroxide dose the kappa number, as an indicator of degree of delignification, reduces but not the viscosity. This finding confirms the selectivity of the acidic peroxide delignification.

The mechanism of lignin removal during acidic peroxide stage has not yet been fully elucidated. In the unbleached pulp, the aromatics and the polysaccharides are covalently bonded together intimately. The delignification of the residual lignin is made

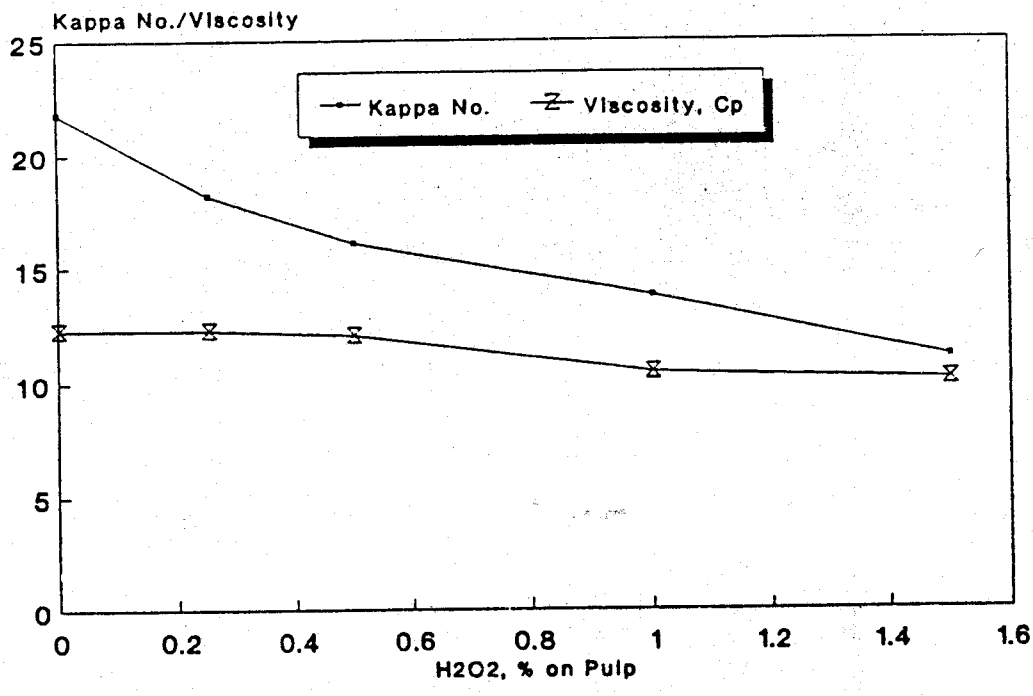

Fig-1. Selectivity of Acidic Hydrogen Peroxide on Delignification.

difficult because of the size of the lignin molecule connected with polysaccharide molecule by covalent bond. Still, the delignification can be initiated by the differences found in the chemical properties in lignin molecule. Hydrogen peroxide is a highly versatile and effective Phenol oxidant (9). In acidic medium as an electrophile it oxidises lignin by first demethylation, ortho-and para quinone formation and finally the oxidized aromatic ring cleaves and gets dearomatized to low molecular weight dicarboxylic acids and thus the lignin molecule is ready to be solubilized. Hence, in acidic medium hydrogen peroxide is said to behave as delignifying agent. This delignifying ability of hydrogen peroxide has become widely recognized and it is used as a lignin reactivation pretreatment before going for bleaching by more powerful oxidants(10). It is suggested that washing after the acid peroxide treatment may not be necessary(11). Extending the bleaching under optimised conditions upto the final (APCEHH) hypo stage with washing and without washing (data not shown) did not affect the brightness achievement.

Influence of Catalyst

The influence of catalysed peroxide delignification was studied by dosing various quantities of sodium molybdate. The influence of catalysed peroxide delignification was studied by giving different charges of sodium molybdate. The study revealed that uncatalysed peroxide delignification was not efficient. Poor redcuction in the kappa number further substantiates this observation. This is attributed to the poor consumption of hydrogen peroxide. On increasing the catalyst dose from 0 to 1000 ppm, the peroxide consumption considerably increased **(Fig.2).** Similar trend was observed with other pulps as well (12). Therefore, we postulate that for effective delignification not only the peroxide charge, but also its consumption plays a vital role **(Fig.3).** It is a well attested fact that the effibiency of the hydrogen peroxide delignification is enhanced by metal catalysts of molybdenum and tungsten (10,12). These catalytically activated acid peroxide species act as organic peroxy acids which are strong oxidizing agents (9).

Influence of Temperature

Temperature is a very important parameter in acidic peroxide delignification. Initially, an attempt was made to minimise temperature. This resulted in the poor consumption of hydrogen peroxide, and led to poor bleaching effect **(Fig.4).** Hence, the temperature is very crucial in the AP stage and hence could not be compromised. Treatment at various temperatures gave the optimum temperature required. Thus the critical temperature for acidic peroxide delignification is arrived at 85°C.

Effect of Time on Acidic Peroxide Treatment

The study revealed that the minimum time required for optimum consumption was 60 min, beyond which there was very little improvement in the consumption **(Fig.5).**

Molybdenum catalysed acidic peroxide pretreatment was able to produce a pulp with significant improvement in brightness. The major benefit of acid peroxide delignification is the reduction of chlorine and hence in the environmental impact of bleaching. The elemental chlorine was substantially reduced because of the low kappa number. Unfortunately, in the Indian context chlorination is still the preferred first step in the multi-stage bleaching of pulps. So, the high chemical cost of hydrogen peroxide (1%w/w) and molybdate as the catalyst in these studies limit the potential commercial feasibility of the AP system. For these reasons, the second option of introducing the hydrogen peroxide in extraction stage was pursued.

ALKALINE PEROXIDE EXTRACTION

Optimization of the Peroxide Addition in the E stage

Peroxide reinforced oxidative extraction was carried out by adding different doses of peroxide (0.3%, 0.5%, 0.8%, 1.0%). The peroxide charge required to reach target brightness of 85% ISO with CEHH bleaching was taken as the optimum dosage. As the results show **(Table-3),** on increasing the dosage there is a steady state improvement in the pulp extraction as evidenced by the brightness and kappa number. But, increasing the peroxide dosage beyond 0.5%, though had significant influence on the extracted pulp brightness and kappa number, it was not felt in the final bleached pulp brightness. Beyond 0.5% peroxide addition, there is no significant enhancement of brightness after the hypo stage. In the alkaline conditions it has been firmly established that the perhydroxyl anion takes an active part in the bleaching. The perhydroxyl anion (OOH-) oxidises the colour and renders the pulp with increased brightness. Under the alkaline conditions, only unetherified phenolic nuclei or monomer unit having side chains containing a carbonyl group appers to be susceptible to attack (13). Thus, in strong alkaline conditions peroxide favours brightening of pulp rather than delignification (14).

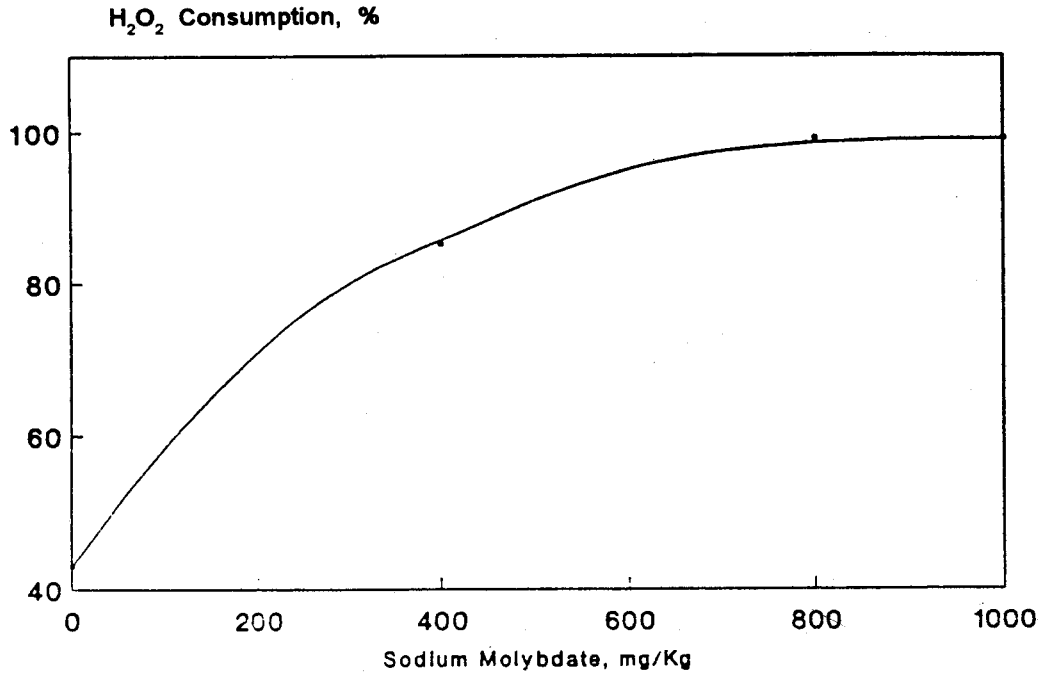

Fig-2. Role of Sodium Molybdate Catalysed Delignification on Peroxide

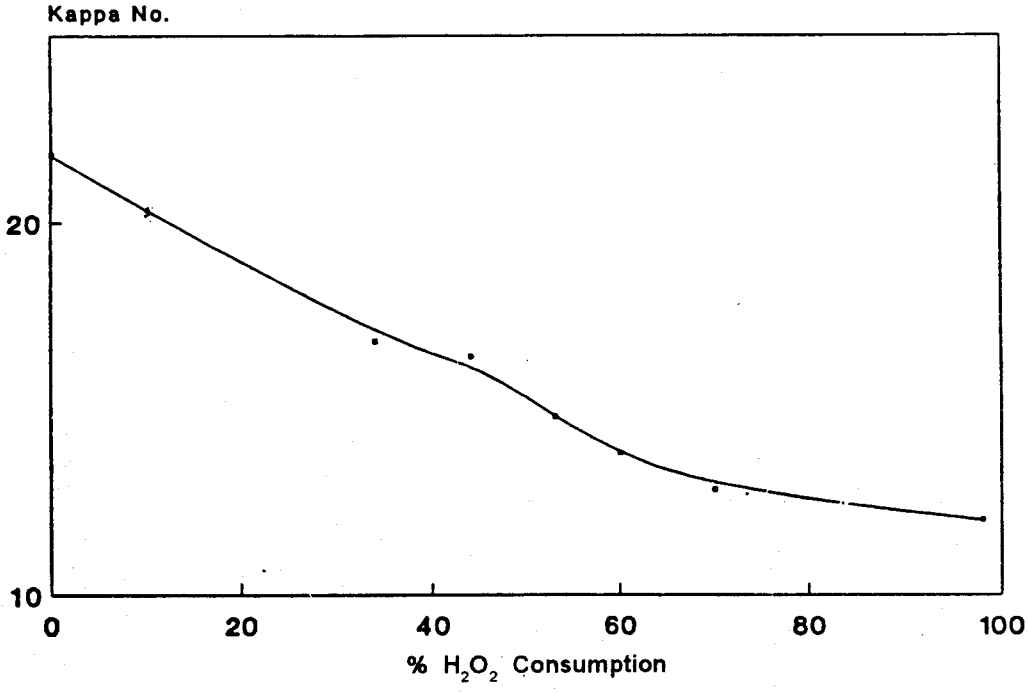

Fig-3. Effect of Acidic Peroxide Consumption on Delignification.

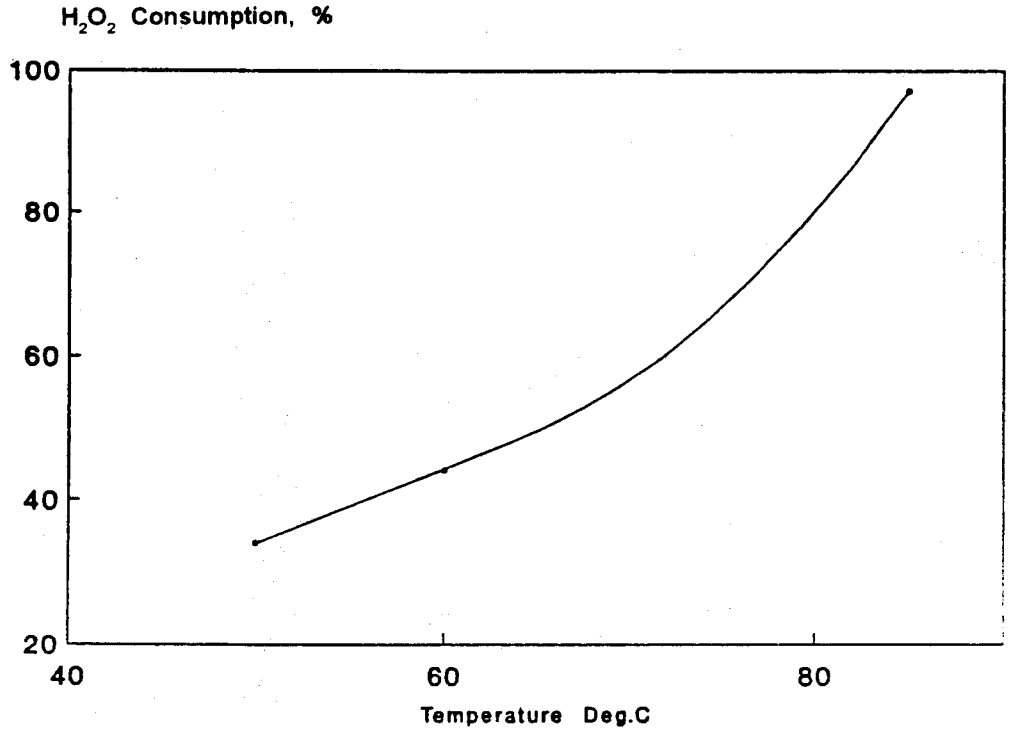

Fig-4. Significance of Temperature on Acidic Peroxide Consumption.

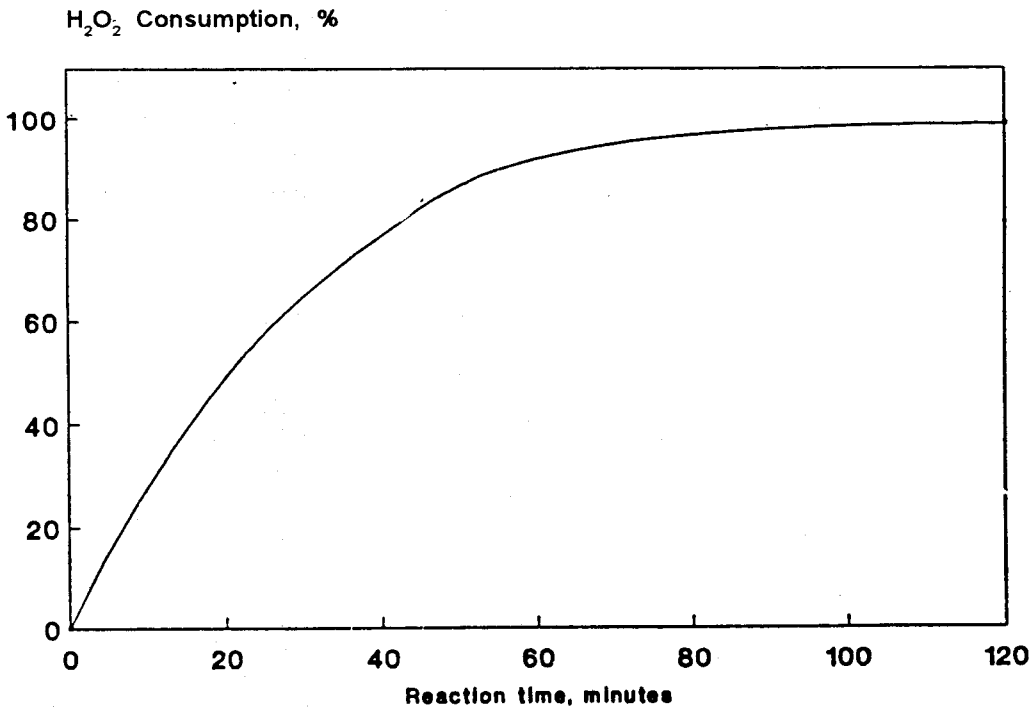

Fig-5. Influence of Reaction Time on Acidic Peroxide Consumption.

Table-3

Effect of varying Alkaline Peroxide application in the oxidative extraction of Kraft Pulp

Chlorination
Applied as Cl_2 % 3.10
Consumed as Cl_2 % 2.92

	1	2	3	4	5
NaOH charge, %	2.0	2.0	2.0	2.0	2.0
H_2O_2 charge, %	-	0.3	0.5	0.8	1.0
CE Brightness, % ISO	40.1	47.4	52.2	56.2	58.5
CE Kappa number	3.6	2.9	2.6	2.3	1.8
CE Viscosity, CP	10.8	9.3	8.5	8.2	7.9
CE Filtrate colour Kg/T Pt. Co. units	49.4	47.1	38.8	35.3	33.4

ACID PEROXIDE VS ALKALINE PEROXIDE -AP VS E(P)

The acidic peroxide delignification and the alkaline oxidative extraction were able to enhance the brightness considerably when compared to the conventional process **(Fig.6)**. However, like oxygen delignification, elemental chlorine demand of AP pulp entering a subsequent chlorination stage is reduced in proportion to the kappa number reduction. Hence, the use of AP brings out a stronger effect on delignification, while E (P) mainly accounts for the removal of colouring groups. AP pretreatment is one of the most effective ways of decreasing the chlorinated organics in the effluents from bleaching, because lesser the delignification required in the C stage, the lesser will be the chlorine requirement. E (P) stage contributes for the reduction of effluent colour (Table-3). It has also been reported that employing peroxide enhanced bleaching strategy, can reduce the dioxin level in the filtrate (15).

The pulp quality, in terms of strength properties, of the AP and E (P) pulps seems to remain unaffected when compared to the reference CEHH bleaching in spite of the enhanced brightness **(Fig.7)**. This gives further impetus for using AP and E (P) in the plant. It can be noted that even though there is regular improvement in the brightness after E (P) for different dosages of peroxide, this is not felt in the final brightness **(Fig.8)**. Incidentally, it was observed that both the AP and E (P) treated pulps showed approximately 10% increase in the scattering power over the traditional CEHH bleaching. (Data not shown).

Retrofitting E (P) in the plant seems to be more viable than AP for achieving high brightness (85% ISO). E (P) does not need any catalytic pretreatment like in AP and requires less amount of hydrogen peroxide (0.5% w/w). High temperature requirement in AP also is not an attractive proposition from the plant point of view. In E stage, Peroxide solution can be mixed with the sodium hydroxide and put in the pulp and hence it is a quick and easy process to implement.

The cost of production is increased substantially in the AP system compared to E (P) because of the sodium molybdate catalyst as well as higher peroxide charge (1% w/w).

With all this background, oxidative extraction reinforced with peroxide gains an upper hand for achieving high brightness of the hardwood kraft pulp.

MILL EXPERIENCE

Since the laboratory reinforced alkaline peroxide extraction studies produced encouraging results, mill trials were performed. As the laboratory experience indicated, peroxide addition was maintained at 0.5-0.6%. Mill experience closely paralleled the laboratory studies. Bleaching of the control sample was carried out under identical conditions except for the exclusion of peroxide. Hydrogen peroxide was added along with the sodium hydroxide in the repulper to enhance the thorough mixing.

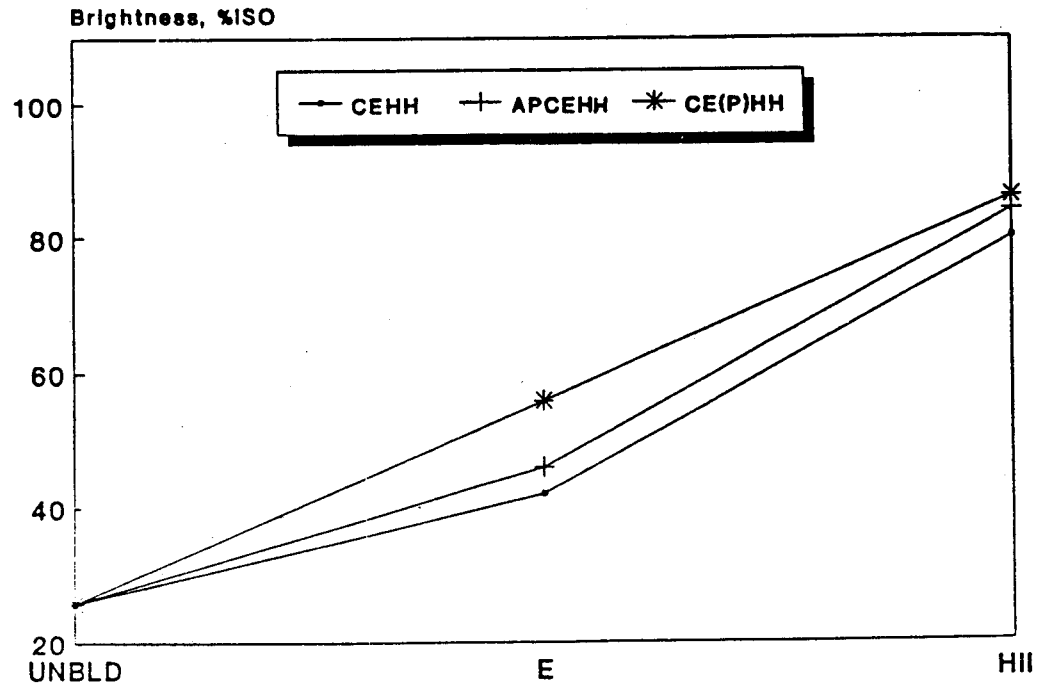

Fig-6. Pulp Brightness (%ISO) Achieved with APCEHH and CE(P)HH Sequences.

Mill runs successfully met the target of high brightness. Brightness of peroxide treated pulp reached 85.0% ISO compared to 79% ISO for the control, with half of the hypo requirement. Brightness gain after the E (P) stage over the blank E stage was substantially high (18 points). There was no apparent loss in the fibre strength as a result of the treatment. Application of hydrogen peroxide in the E stage

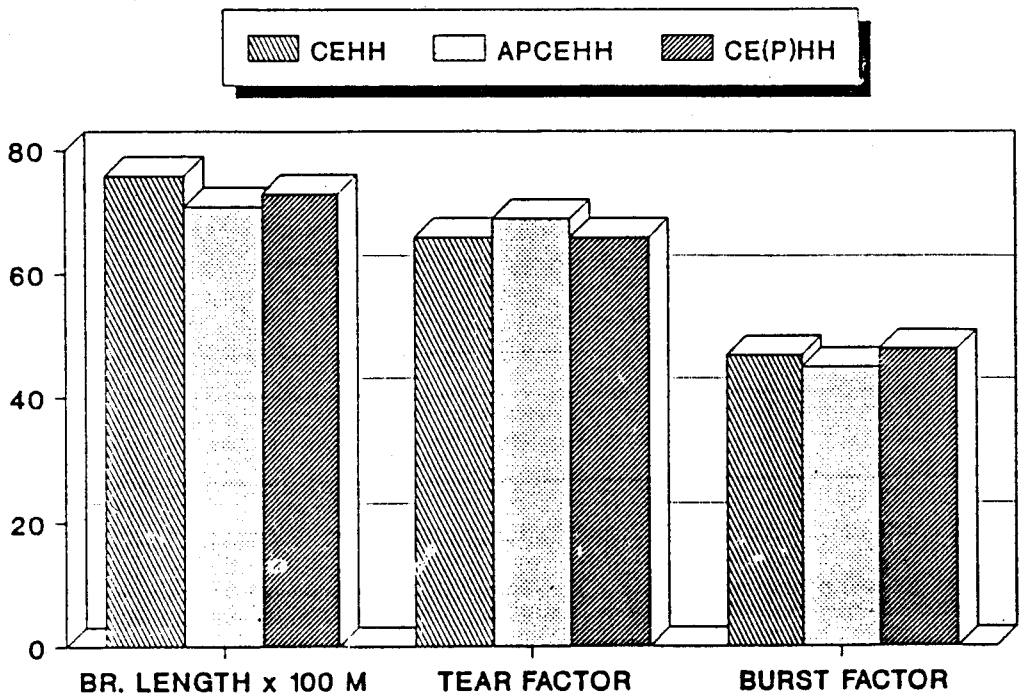

Fig-7. Strength Properties At 300ml CSF.

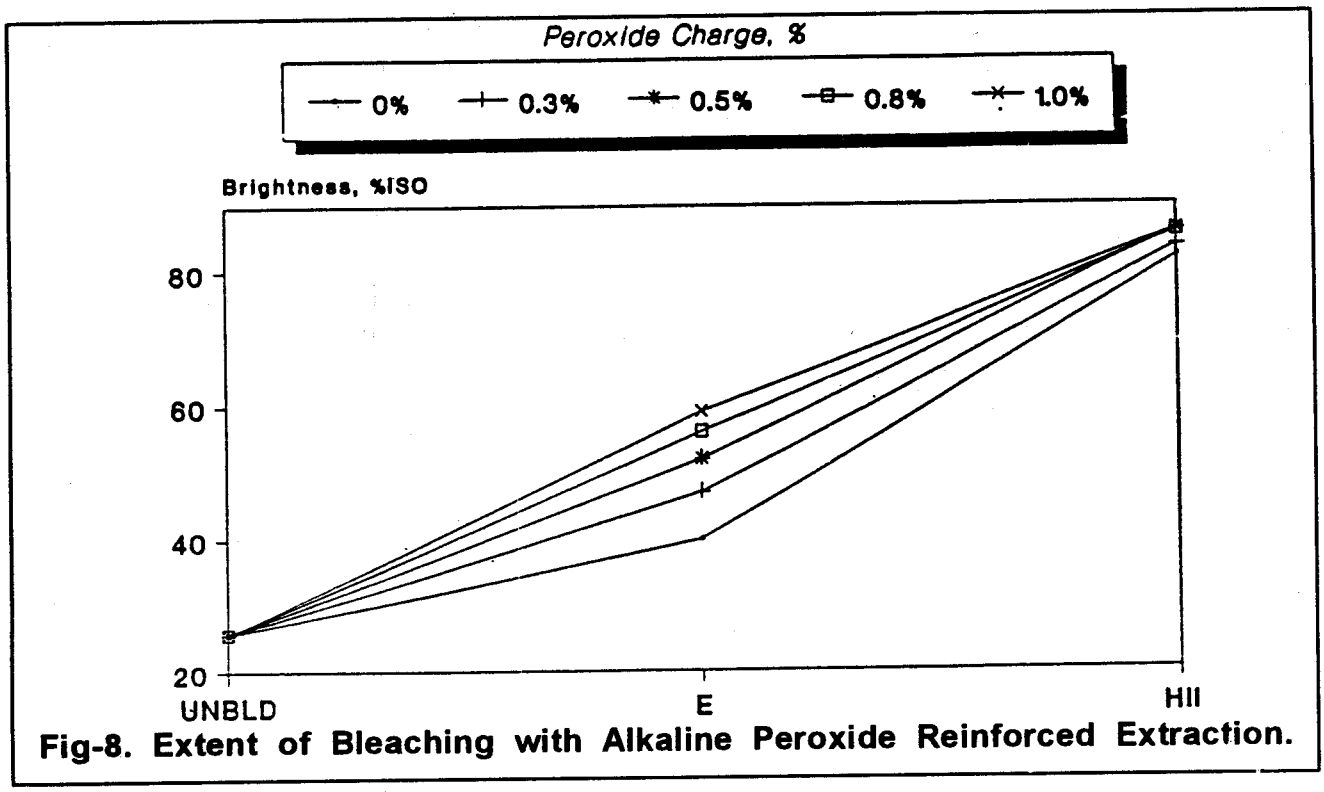

Fig-8. Extent of Bleaching with Alkaline Peroxide Reinforced Extraction.

reduced the colour of the effluent (about 50%). The overall results obtained from the mill scale trials are presented in **Table-4.**

ACKNOWLEDGEMENTS

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Table-4

Mill Trials : Conditions and Results

Screened Unbleached Kappa No. : 20

Screened unbleached brightness : 23 % ISO

	Kg/bdmt H_2O_2 in E-stage	Kappa No. after E-stage	Brightness (% ISO) after E-stage	Kg/BDMT Hypo as active Cl_2	Final Brightness % ISO	Final Viscosity cP.S
Blank	--	5.1	36.6	32.6	79.4	4.6
Trial	6.1	3.2	54.9	16.1	85.3	4.4

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