Studies on peroxide bleaching of kraft pulps

J.S. UPADHYAYA,* RANVEER SINGH,*
DIGVIJAY RAWAT* AND
ANIL PANT*

ABSTRACT

In the present communication, the application of hydrogen peroxide in CEHP and CEpH bleaching sequences of kraft pulps were studied The results indicated that CEpH bleaching sequence is far better than CEHP bleaching sequence. The maximum increase in brightness was observed at a pH of approximately 11, at the commencement of alkaline extraction. The presence of sodium silicate helps in stabilishing peroxide during alkaline extraction. A high pulp consistency and a high temperature was found to be favourable for bleaching. The most actractive feature of a peroxide bleached pulp was its low brightness reversion.

INTRODUCTION

Now-a-days, the requirement of pulp with high degree of brightness is increasing day-by-day. The unbleached kraft pulps normally have a brightness of 15 to 30% (G.E.), and the exact value has very little, if any, bearing on the final brightness reached. Their bleaching requires more chemicals and more stages than that of sulphite pulp. The brightness gap between unbleached and fully bleached kraft pulp is about 60% (G.E), has led to the introduction of an intermediate semibleached product. Its brightness range is not clearly defined and appears to change with progress in bleaching. Originally it covered approximately the range 60 to 70% (G.E.), but since the introduction of new bleaching agents, the upper limit has been pushed close to 80% (G.E.)[1]. The dominant sequence to produce such semi-bleached pulp, is CEH, which may be specially installed for this purpose or may be the front section of a longer sequence with facilities to withdraw part of the production, primarily for newsprint.

Kraft/soda pulps are generally bleached by either CEH or CEHH bleaching sequence. During chlorination of pulp, chlorolignins are formed. These chlorolignins are extracted during alkaline extraction stage, when these chlorinated compounds are dissolved/extracted, the colour of the pulp becomes darker. The main objective of extraction stage (E) is to make the pulp ready for subsequent oxidative bleaching (generally hypochlorite). However, this particular period is not actually used for bleaching and is therefore considered as a dead period. By introducing hydrogen peroxide in an alkaline extraction stage, this dead period can be utilized to improve the brightness of the pulp. Due to alkaline extraction of chlorinated pulp, Kappa/permanganate number of pulp reduces and it becomes easier to bleach further with hypochlorite. Sometimes, the pulp mill faces a problem of variation in quality of raw material or problem of temporary irregularities in cooking operation. However, under such flexible operations of the mill, by introducing hydrogen-peroxide at the extraction stages, the brightness level can sometimes be adjusted. Moreover, the effluent coming out at the extraction stage also has less colour when hydrogen peroxide is used during extraction.

*University of Roorkee,
Institute of Paper Technology,
Saharanpur - 247 001.

The kraft bleach plants have a common need to produce brighter pulp with better brightness stability. Hydrogen peroxide has been considered as an ideal reagent for the same reason-to stabilize and hold the brightness to a maximum degree against the reversion commonly encountered from the heat of refining and heat drying over the paper machine or the pulp sheet dryer 2-4.

Because of high price of peroxide, its use for bleaching chemical/kraft pulps is not so wide-spread. For kraft pulps[5], the hydrogen peroxide can be added either in an alkaline extraction stage or it can be used as a separate final bleaching stage. In the present investigation, the comparative studies of both aspects of addition of hydrogen peroxide during alkaline extraction as well as a separate final bleaching stage after CEH bleaching sequence were conducted on wood-non wood (Eucalyptus-Bamboo) blended kraft pulps.

Methodology and Strategies for Experimental Design

Since our studies are concentrated on comparative effects of addition of hydrogen peroxide either in CEpH or CEHP bleaching sequences; therefore the main variables are doses of chlorine (and its distribution between chlorination and hypocolorite stage), alkali, hypochlorite and hydrogen peroxide, used during both the bleaching sequences In addition to these, other variables include the pH, temperature, time and consistency of the system. Therefore, the present investigation is a multivariable problem, and factorial design method is used in such conditions. The dose of chlorine was fixed based on Kappa number of unbleached pulp, 70% of which was applied during chlorination and 30% during hypochlorite stage. The other variables like temperature, pH, time and consistency of the system, depend on a particular bleaching stage. Therefore, the various input and output variables includes :

Input variables :

- dose of sodium hydroxide (NaOH)
- dose of hypochlorite and
- dose of hydrogen peroxide.

Output control parameters :

- brightness of pulp
- physical strength properties of pulp
- post colour number of pulp.

In the input variables, the dose of NaOH is dependent on the pH of the system. Fixing six dose levels for H_2O_2 and three dose levels for hypochlorite, the total number of experiments comes out to be eighteen (18) in each series of bleaching sequences; to optimise the dose of H_2O_2 and hypochlorite.

Materials and Methods

During bleaching of pulps, as a general practice all pulps were diluted with distilled water and the temperature adjusted so that after mixing with chemicals, the consistency would be as stated and the pulp suspension would be at or quite near the bath temperature required for the purpose. All additions of chemicals were on the basis of the oven dry weight of pulp entering to that particular stage.

The bleaching experiments were done in polyethylene bottles using distilled water and chemicals of analytical grade. At higher consistency, poloyethylene bagas were used in order to facilitate mixing at bleaching temperature. The bleached pulp samples (CEHP sequence) were after treated with 1% SO_2 water for 15 minutes. At the end of each stage pulps were collected on hard filter paper in Buchner funnels, all pulps being washed with distilled water. After chlorination and hypochlorite stages, washings were done with cold water followed by water at about 60°C, whereas after alkali extraction or peroxide, the reverse procedure was followed. The output control parameters viz., brightness, post colour number and physical strength properties were determined according to TAPPI methods. (Freenss level, 40° SR; gsm of sheet, 60).

CEHP Sequence :

The various bleaching data and process conditions in CEH stages are reported in Table-I. The CEH treated pulp was again exposed to different doses of hydrogen peroxide (0.2-1.0%) at a pH level of 11.1. The various doses of alkali required to maintain desired level of pH alongwith other process conditions and pulp evaluation data are reported in Table-II. After optimising the dose of peroxide (0.4%), the effect of addition of different doses of chlorine (0.5 to 3.5%) during hypochlorite stage, on brightness, and colour reversion was studied and the results are recorded in Table-III.

Table—I : Bleaching data and Process Conditions* during CEHP Sequence.

Sl. No.	Particulars	Values
1.	Kappa number of unbleached pulp.	32 83
2.	Chlorine demand, %	8.21
3.	Chlorine applied during chlorination, (as available chlorine), %	6.00
4.	Alkali applied during alkaline extraction, %	1.5
5.	Chlorine applied during hypochlorite (as available chlorine), %	3.5
6.	Brightness of unbleached pulp (Elrepho), %	21.2
7.	Brightness of chlorinated pulp (Elrepho), %	28.3
8.	Brightness of extracted pulp (Elrepho), %	30.4
9.	Brightness of pulp after H stage (Elrepho), %	67.2

*Process Conditions	C	E	H
Consistency, %	3.5	9.0	9
Retention time, min.	45	90	180
Temperature, °C	Ambient	60	Ambient
pH	2.0	11.1	10.5

Table—II : Doses of alkali required with different doses of H_2O_2 to maintain a pH level of 11.1 alongwith process conditions* (during P stage) and pulp evaluation data.

Sl. No.	Peroxide applied % (O.D. pulp basis)	alkali required % (O.D. Pulp-basis)	Brightness %(Elrepho)	Colour Reversion,%	Tensile Index	Tear Index	Burst Index	Folding Endurance
1.	0.2	1.0	72.4	4.3	65.30	2.6	4.38	98
2.	0.4	1.2	74.8	3.6	65.41	2.6	4 37	97
3.	0.6	1.4	75.1	4.1	65.33	2.6	4.35	96
4.	0.8	1.6	75.5	5.3	65.20	2.6	4.30	95
5.	1.0	1.8	75.7	5.3	64.90	2.6	4.25	95

*Process Condition : Consistency 9%,
Retention time 120 min.,
Temperature 65° C,
pH 11.1

Table—III : Effect of different doses of hypochlorite (as available chlorine %) during hypochlorite stage alongwith other process conditions*. (CEHP Sequence)

Sl. No.	Hypochlorite dose applied % (as available chlorine)	Brightness, % (Elrepho)	Colour reversion, %	Tensile Index	Tear Index	Burst Index	Folding Endurance
1.	3.5	74.8	3.6	65.41	2.6	4.38	90
2.	3.0	72.4	4.3	64.92	2.9	4.24	91
3.	2.5	69.1	4.9	62.93	2.6	4.06	83
4.	1.5	64.8	5.3	59.81	2.6	3.84	72
5.	1.0	61.2	6.0	52.73	2.3	3.55	67
6.	0.5	47.7	7.8	45.21	1.9	3.25	59

*Process conditions : Consistency—9%, retention time—180 min., Temperature-Ambient, pH 10.5

Table –IV : Effect of different doses of peroxide added during alkaline extraction stage alongwith other process conditions*.

Sl. No.	Peroxide added %, (O.D. Pulp basis)	Brightness after Ep stage	Final Brightness %, (Elrepho)	Colour reversion, %	Tensile Index	Tear Index	Burst Index	Folding endurance
1.	0.2	42.6	74.5	1.60	67.00	2.6	4.85	108
2.	0.4	47.7	79.9	1.50	67.20	2.6	4.87	108
3.	0.6	52.5	81.0	1.55	67.15	2 6	4.85	107
4.	0.8	57.2	81.4	1.65	67.20	2.6	4.80	106
5.	1.0	61.3	81.5	1.70	67.00	2.3	4.75	105

*Process Conditions : Magnesium sulphate 0.1%, sodium silicate 5%

	C	Ep	H
Consistency, %	3.5	9	9
Retention time, min.	45	90	180
Temperature, °C	Ambient	60	Ambient
pH	2.1	11.1	10.7

Table—V : Effect of different doses of hypochlorite (as available chlorine, %) during hypochlorite stage alongwith other process conditions.*(CEpH sequence).

Sl. No.	Hypochlorite dose applied, % (as available chlorine)	Brightness, % (Elrepho)	Colour reversion %	Tensile Index	Tear Index	Burst Index	Folding endurance
1.	3.5	79.9	1.50	67.23	2.6	4.87	108
2.	3.0	78.4	1.55	67.21	2.6	4 63	103
3.	2.5	75.8	1.60	65.32	2.3	4.51	90
4.	1.5	68.3	1.67	60.14	2.3	4.32	91
5.	1.0	62.3	1.70	57.21	1.95	4.16	81
6.	0.5	48.8	1.82	51.21	1.95	3.87	73

*Process conditions : Consistency — 9%,
Retention time — 180 min.,
Temperature — Ambient
pH — 10.5

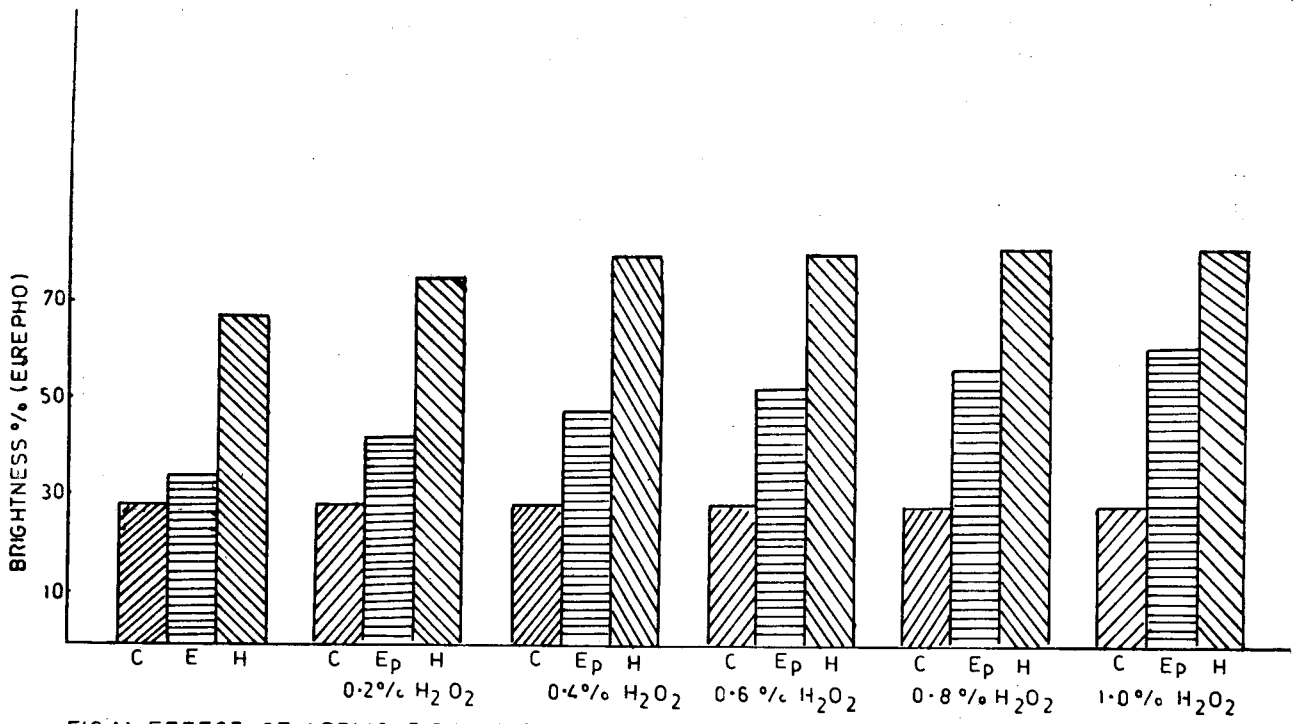
CEpH Sequence

The chlorinated pulp was washed, dried and treated with 1.5% alkali (pH around 11) and different doses of hydrogen peroxide (0.2 to 1.0%) in presence of 0.1% magnesium sulphate and 5% sodium silicate, (to enhance the stability of hydrogen peroxide). The Ep extracted pulp samples were further subjected to hypochlorite solution (3.5% available chlorine). The bleaching data and process conditions are reported in Table-IV. After optimising the dose of peroxide (0.4%) during alkaline extration,the CEp extracted pulp samples were treated with different dose of hypochlorite (0.5 to 3.5%, as available chlorine) to study their effect on brightness, colour reversion and other strength properties and the results are reported in Table-V.

Results and Discussion

The brightness values were recorded at unbleached pulp stage, final stage and after each of the intermediate bleaching stage, Figure-2 shows that by changing the bleching sequence from CEHP to CEpH, a higher level of brightness was achieved. The improvement in brightness is directly proportional to the amount of peroxide added during alkaline extration stage, but the magnitude of increase in brightness was observed to be higher at lower doses of peroxide and afterwards this magnitude of increase in brightness was not so pronounced as observed earlier. By using 0.2 to 1.0% peroxide doses (Figure-1), the brightness values of pulps after CEp stage were found 12.6 to 31.3% (Elrepho) higher than that of CE bleached pulp. This indicates that hodrogen peroxide performs a role af purifying the chlorinated pulp at alkali extraction stage and thus enhances the brightness level of pulp.

The quantity of peroxide used during extraction stage plays a vital role for enhancing the brightness. As the hardness of the pulp increases (high Kappa number) higher chlorine doses are required at chlorinntion stage. This leads to the formation of large quantity of chlorolignins, which requires lot of alkali for dissolving chlorolignins thereby the colour of the pulp looks darker. The treatment of such pulp requires large quantity of peroxide to observe any visible effect, and it would be perhaps uneconomical. Secondly, the effect which was observed by using peroxide during alkaline extraction, however decreases in subsequent stage of bleaching. It is possible to obtain increased brightness with an increase in the amount of added hydrogen peroxide, but the brightness increase gained by the additional hydrogen peroxide will be the smaller the greater the total amount of added hydrogen peroxide. It is therefore not advisable to use large quantity of hydrogen peroxide during alkaline extraction stage.



FIG·1; EFFECT OF APPLICATION OF DEFFERENT DOSES OF HYDROGEN PEROXIDE DURING ALKALINE EXTRACTION STAGE ON BRIGHTNESS.

Hydrogen peroxide decomposes rapidly at pH values around 12, whbreas it is too stable at little lower pH values. The pH zone of 11.5 to 9.5 is quite suitable for hydrogen peroxide to be effective. It was observed that for the addition of peroxide during alkaline extraction stage, the initial pH should be maintained around 11, so that one can get a final pH of around 10 at the end of extraction. Therefore the quantity of alkali is reduced in most of the cases at extraction stage, when peroxide is incorporated. Sodium silicate, which imparts alkalinity and also acts as buffer, plays the role of stabilising peroxide at alkaline extraction stage.

The temperature during Ep stage also plays a vital role in affecting brightness. Higher the temperature. better are the bleaching effects with peroxides. However, the temperature should not be more than 70°C, as the very high temperature may decompose hydrogen peroxide under alkaline conditions. In the alkaline extraction stage, even under ambient conditions, one can get excellent results.

The retention time depends upon temperaturee. Higher the temprature, the lower will be the retention time. However, a retention time of 60 to 120 minutes is generally sufficient. Hydrogen peroxide is most effective at higher consistency. However, a consistency level of 5 to 10% could also be sufficient.

The colour reversion tendency was found to be higher for pulps bleached by CEHP bleaching sequence than for the pulps bleached by CEpH bleaching sequence. The colour reversion tendency increases with an increase in brightness of pulp samples.

The strength properties of pulps bleached by CEpH bleaching sequence showed higher values than the pulps bleached by CEHP bleaching sequence. Irrespespetive of bleaching sequences, the peroxide bleaching has been found to have little effect upon pulp properties as well as pulp yield. The bulk, strength properties and freeness remains almost unchanged. The opacity, which would be expected to be lower because of the increased brightness, is slightly increased. Although the strength properties are not much affected by peroxide bleaching even though a very little drop was observed at higher doses of peroxide (Fig.3 to 5). The reason of peroxide for not affecting the strength properties is simple that peroxide is a lignin preservating bleaching agent. It simply reacts with chrmophoric groups to

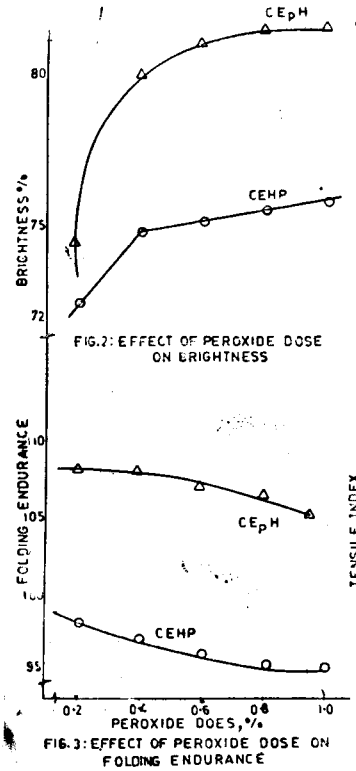


FIG.2: EFFECT OF PEROXIDE DOSE ON BRIGHTNESS

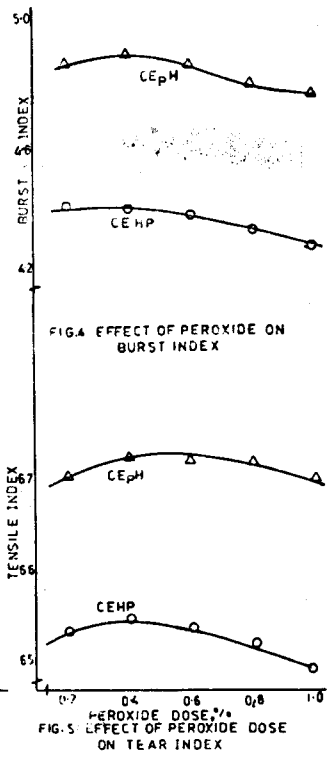


FIG.4 EFFECT OF PEROXIDE ON BURST INDEX

FIG.3: EFFECT OF PEROXIDE DOSE ON FOLDING ENDURANCE

FIG.5 EFFECT OF PEROXIDE DOSE ON TEAR INDEX

decolourise them without their removal. However, at higher peroxide doses, some undesirable reactions take place, thereby affecting the yield as well as strength properties.

In order to achieve, a particular brightness level with peroxide, hypochlorite dose can be reduced correspondingly. This reduction would reduce the pollution load of effluent and increase the viscosity of pulp. Based on experimental results, the economics favour the use of CEpH bleaching sequence over CEHP bleaching sequence.

Conclusions

The conventional bleaching sequences like CEH or CEHH of soda/kraft pulps can be improved by introducing hydrogen peroxide during alkaline extraction stage rather than using hyderogen peroxide as a last stage of conventional bleaching sequence i.e. CEHP.

The use of hyderogen peroxide during alkaline extraction stage-substantially increases the brightness and reduces the colour of effluent. The quantity of hydrogen peroxide to be introduced during alkaline extraction stage depends on the type of pulp, cooking conditions and extent of chlorination etc. Generally 0 25% to 0.75% hydrogen peroxide on oven dried pulp basis, is sufficient during alkaline extraction stage.

The maximum increase in brightness was observed at a pH slightly above 11 at the commencement of alkali extraction and at the end of extraction it should be around 10 The use of peroxide during alkaline extraction stage is thus a very simple and effective way of improving the (brightness of pulp without affecting other physical strength properties of pulp) conventional bleaching of kraft and soda pulps.

References :

1. G.A. Nicholls, Tappi 43 (11), 910 (1960).
2. S.R. Tendulkar, IPPTA 23 (2), 1 (1986).
3. R.S. Kouk & P. Meyrant Paper presented at 3rd Jugoslovenski Simpozijum O Celulozii Papiru, UNICEP Zbornik Radova, Banjaluka April 14-15, 1987.
4. M. Hoyos & P. Meyrant, Paper presented at ESPRA Meeting Charlottle, N.C. March 29-April 2, 1987.
5. N. Hartler, E Lindahl, C. Moberg and L. Stockman, Tappi 43 (10), 806 (1960)