Elemental Chlorine Free Bleaching of Bagasse Chemical Pulp

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INTRODUCTION

As an alternative to the forest based raw materials to meet the increasing shortfall of furnish such as hardwood and bamboo the paper industry has been considering nonwood fibrous raw material as the chief source of fibres. The main fibrous raw materials available in abundance in India are Bagasse, Rice Straw and Wheat Straw. The Bagasse will continue to play key role even in future as potential raw material for paper industry.

Pulping and bleaching of bagasse is well established in paper industry. The chemical pulp of bagasse is considerd to be easy to bleach. By and large, bagasse chemical pulp is bleached by usage of CEH or CEHH (1, 2, 3) bleaching sequence. Since the introduction of peroxide reinforced alkali extraction in India, many paper mills have switched over to CEpH type of bleaching sequence (4, 5). This bleaching sequence has resulted in improvement of brightness of bagasse pulp without sacrificing the strength of pulp in many paper mills.

During bleaching of kraft pulp, a significant amount of organic material is dissolved in chlorination and extraction stages. When chlorine is used to bleach the pulp, some dissolved organic matter in bleach plant effluent will contain organically bound chlorine. The discharge rate of organically bound chlorine is approximately 4-5 kg/tonne of pulp. This is measured as Absorbable Organic Halogen (AOX). A lot of literature has been published on the subject (6-10). The best way to reduce AOX in effluent/pulp & paper is to reduce/eliminate usage of chlorine (11-14). The usage of chlorine and chlorine compounds is being phased out due to growing concerned about AOX in developed countries. Many countries have prepared a time bound programme to reduce this rate of discharge of AOX. The technologists are discussing about Reduced chlorine (RC), Elemental Chlorine Free (ECF), Total Chlorine Free (TCF), as well as Total Effluent Free (TEF) bleaching of pulp. Many pulp mills in Europe and USA either due to government regulations or due to market demand have already switched over to ECF or TCF bleaching. The technologies used are based on hydrogen peroxide, oxygen, ozone etc.

The technologies which are being discussed and being used by developed countries are mostly meant for bleaching 500 to 1000 TPD chemical pulp of wood. These technologies may not be technoeconomically feasible for agro residue pulp mills smaller than 100 TPD in developing countries. For bleaching of pulp from agro residue like bagasse rather than going for western ultra modern bleaching technology, one may select Best Available Technology (BAT) locally. Earlier some efforts were made for chlorine free bleaching of bagasse (15).

In this particular presentation attempts have been made to bleach chemical pulp of bagasse by eliminating elemental chlorine totally. Thus Elemental Chlorine Free (ECF) chemical bagasse pulp is being attempted. Apart from ECF bleaching, the objective of this study is to produce pulp with acceptable brightness with excellent brightness stability, Hence instead of CEH bleaching PHP bleaching sequence has been used for chemical bagasse pulp and comparison of both these sequences have been made during this study.

EXPERIMENTAL

Unbleached bagasse chemical pulp was collected from one of the paper mills from South India for this study. The permangnate number of the pulp was 8.8 and its brightness was 41.5 °ISO. This unbleached pulp

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after disintegration in the laboratory disintegrator was squeezed on 200 mesh. This squeezed pulp after determining the consistency divided into two parts.

a. The first part was subjected for CEH bleaching sequence.

b. Second part was subject for PHP bleaching sequence.

The first part was subjected for normal CEH type of bleaching (Table 2 & Fig. 1) which is being a practice in Indian paper mills. The bleaching condition during CEH and PHP sequence are given in Table 1.

Table-1.

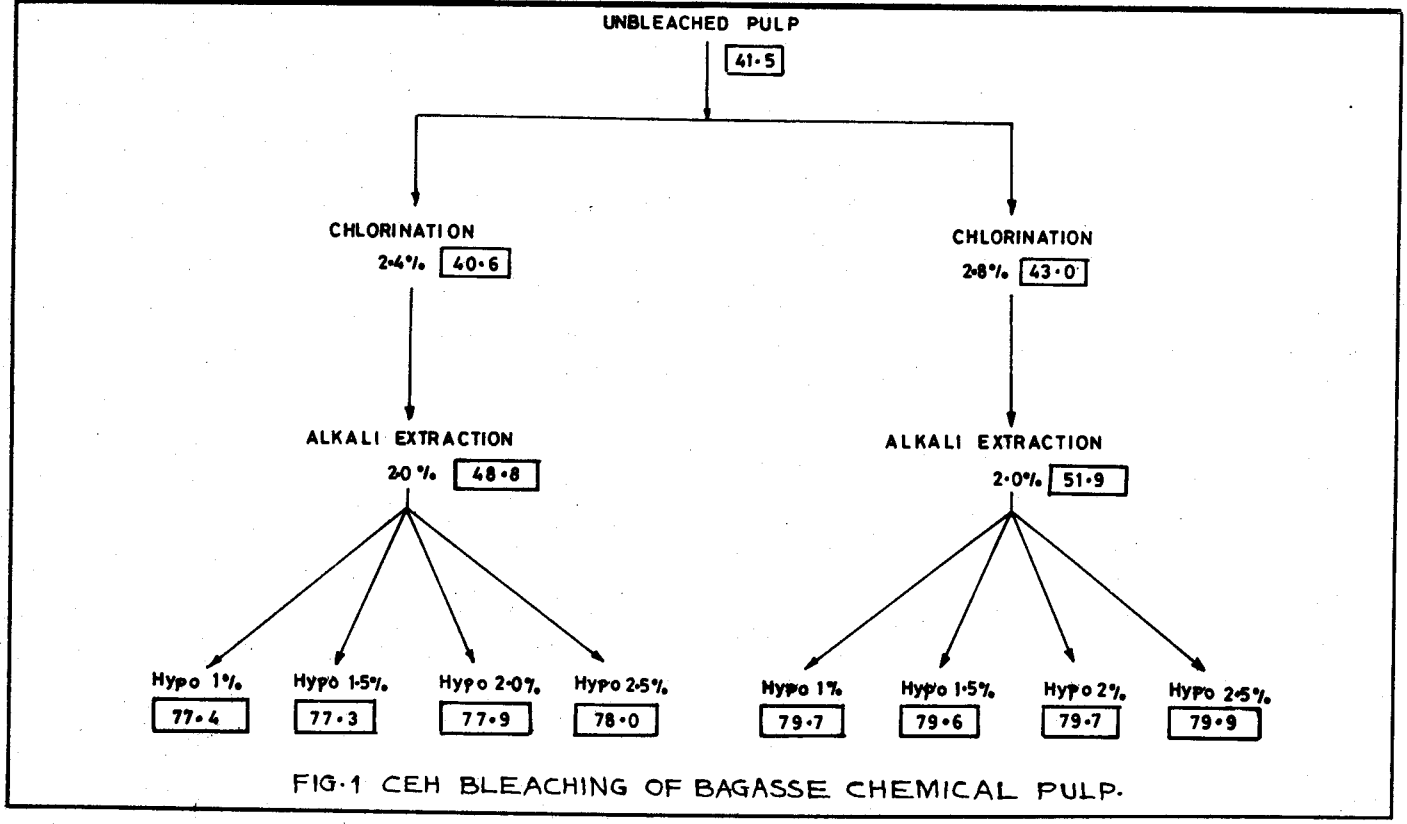
General Bleaching Conditions

Sequence	Consistency %	Temperature 0C	Retention time (min.)
C	2	Ambient	45
E	10	60	60
H	10	Ambient	120
P	10	80	120
H	10	Ambient	120
P	10	80	120

Table-2.

CEH Bleaching of Bagasse Chemical Pulp

SEQUENCE / PARAMETERS	C	E	H_1	H_2	H_3	H_4	C	E	H_1	H_2	H_3	H_4
1. Chlorine (AC) on OD pulp	2.4						2.8					
2. Caustic, % on OD pulp		2.0						2.0				
3. Ca-Hypo (AC) % on OD pulp			1.0	1.5	2.0	2.5			1.0	1.5	2.0	2.5
4. pH final	1.98	11.6	7.8	8.5	9.3	9.6	1.98	11.5	8.1	9.0	9.2	9.7
5. Residual Chemical Cl_2 (gpl)	0.074		0.224	0.56	0.89	1.41	0.074		0.29	0.67	1.04	1.49
6. Brightness, °ISO	40.6	48.8	77.4	77.3	77.9	78.0	43.0	51.9	79.7	79.6	79.7	79.9
7. Reverted brightness, °ISO			69.1	69.3	70.0	70.2			71.3	71.9	72.2	71.4
8. P.C. Number			3.61	3.47	3.29	3.22			3.19	2.88	2.77	3.21
9. Viscosity, CPs			16.2	13.6	12.1	12.4			13.9	13.3	10.2	10.6



FIG·1 CEH BLEACHING OF BAGASSE CHEMICAL PULP.

Second part of the pulp was bleached by PHP type of sequence. Chlorine stage was replaced by alkaline hydrogen peroxide. Various percentages of hydrogen peroxide were used at first stage [0.5-2.0% H_2O_2 (100%) on Pulp]. After peroxide stage pulp was subjected for hypochlorite bleaching (1.5% and 2.0% hypochlorite on available chlorine basis was used at this stage). Thus PH bleached pulp was subjected again for hydrogen peroxide bleaching using dosages given in Table 3 & Fig. 2.

During peroxide bleaching caustic was used as buffer and sodium silicate and magnesium sulphate were used as stabilizers.

Table-3 A.

PHP Bleaching of Bagasse Chemical Pulp

Unbleached Brightness of Pulp = 41.5 °ISO

SEQUENCE / PARAMETERS	$P_{0.5}$	H	P	P	P	$P_{0.5}$	H	P	P	P
1. Caustic, % on OD pulp	0.77		0.4	0.5	0.6	0.77		0.45	0.5	0.65
2. Sodium silicate 38 °Be, % on OD Pulp	2		2	2	2	2		2	2	2
3. $MgSO_4.7H_2O$, % on OD Pulp	0.5		0.5	0.5	0.5	0.5		0.5	0.5	0.5
4. H_2O_2 (100%), % on OD Pulp	0.5		0.5	0.75	1.0	0.5		0.5	0.75	1.0
5. Ca-Hypo (AC) % on OD pulp		1.5					2.0			
6. pH final	9.2	7.52	9.3	9.35	9.5	9.2	7.45	9.36	9.44	9.38
7. Residual Chemical Cl_2 /H_2O_2 (gpl)	0.121	0.04	0.14	0.25	0.32	0.121	0.04	0.16	0.215	0.232
8. Brightness, °ISO	52.5	65.2	72.5	73.3	75.3	52.5	69.5	75.8	76.4	77.3
9. Reverted brightness, °ISO			68.2	69.3	71.2			71.3	71.9	72.4
10. P.C. Number			2.2	1.94	1.77			1.91	1.85	1.93
11. Viscosity, CPs			17.0	16.2	14.6			13.4	13.6	12.6

SEQUENCE / PARAMETERS	$P_{1.0}$	H	P	P	P	$P_{1.0}$	H	P	P	P
1. Caustic, % on OD pulp	0.81		0.5	0.6	0.7	0.81		0.5	0.6	0.7
2. Sodium silicate 38 °Be, % on OD Pulp	2		2	2	2	2		2	2	2
3. $MgSO_4.7H_2O$, % on OD Pulp	0.5		0.5	0.5	0.5	0.5		0.5	0.5	0.5
4. H_2O_2 (100%), % on OD Pulp	1.0		0.5	0.75	1.0	1.0		0.5	0.75	1.0
5. Ca-Hypo (AC) % on OD pulp		1.5					2.0			
6. pH final	9.25	7.7	9.5	9.7	9.7	9.25	7.62	9.31	9.45	9.62
7. Residual Chemical Cl_2 /H_2O_2 (gpl)	0.322	0.04	0.143	0.107	0.125	0.322	0.07	0.161	0.089	0.196
8. Brightness, °ISO	57.2	69.0	75.3	76.2	77.0	57.2	71.8	77.9	78.5	78.4
9. Reverted brightness, °ISO			71.0	71.9	72.8			72.9	74.1	74.4
10. P.C. Number			1.95	1.77	1.65			1.70	1.62	1.43
11. Viscosity, CPs			14.5	15.2	14.7			14.8	13.2	13.1

Table-3 B.

PHP Bleaching of Bagasse Chemical Pulp

SEQUENCE / PARAMETERS	$P_{1.5}$	H	P	P	P	$P_{1.5}$	H	P	P	P
1. Caustic, % on OD pulp	0.9		0.5	0.6	0.7	0.9		0.5	0.6	0.7
2. Sodium silicate 38 ^{0}Be, % on OD Pulp	2		2	2	2	2		2	2	2
3. $MgSO_4.7H_2O$, % on OD Pulp	0.5		0.5	0.5	0.5	0.5		0.5	0.5	0.5
4. H_2O_2 (100%), % on OD Pulp	1.5		0.5	0.75	1.0	1.5		0.5	0.75	1.0
5. Ca-Hypo (AC) % on OD pulp		1.5					2.0			
6. pH final	9.3	7.71	9.51	9.52	9.52	9.3	7.62	9.59	9.62	9.6
7. Residual Chemical Cl_2/H_2O_2 (gpl)	0.453	0.04				0.453	0.112			
8. Brightness, ^{0}ISO	60.0	71.3	76.1	77.3	78.1	60.0	73.3	77.8	79.2	79.2
9. Reverted brightness, ^{0}ISO			72.0	73.3	74.1			73.5	75.0	75.3
10. P.C. Number			1.70	1.53	1.45			1.61	1.43	1.32
11. Viscosity, CPs			14.1	13.9	14.3			13.1	12.6	12.6

SEQUENCE / PARAMETERS	$P_{2.0}$	H	P	P	P	$P_{2.0}$	H	P	P	P
1. Caustic, % on OD pulp	1.0		0.5	0.6	0.7	1.0		0.55	0.6	0.7
2. Sodium silicate 38 ^{0}Be, % on OD Pulp	2		2	2	2	2		2	2	2
3. $MgSO_4.7H_2O$, % on OD Pulp	0.5		0.5	0.5	0.5	0.5		0.5	0.5	0.5
4. H_2O_2 (100%), % on OD Pulp	2.0		0.5	0.75	1.0	2.0		0.5	0.75	1.0
5. Ca-Hypo (AC) % on OD pulp		1.5					2.0			
6. pH final	9.35	7.75	9.35	9.71	9.75	9.35	7.65	9.71	9.62	9.6
7. Residual Chemical Cl_2/H_2O_2 (gpl)	0.59	0.07				0.59	0.14			
8. Brightness, ^{0}ISO	61.3	72.5	76.8	78.1	78.5	61.3	74.3	78.7	79.0	79.3
9. Reverted brightness, ^{0}ISO			73.2	74.2	74.7			74.7	75.2	75.4
10. P.C. Number			1.40	1.41	1.34			1.18	1.29	1.31
11. Viscosity, CPs			13.5	13.1	13.0			11.2	15.2	11.0

In order to study the impact of bleaching on bleaching shrinkage CEH and PHP sets were selected such a way that their reverted brightness values after ageing test were almost of same order.

Mechanical properties such as tear factor, burst factor and breaking length were studied at 40^0 SR for both CEH and PHP bleached pulp - Table 4.

TESTING

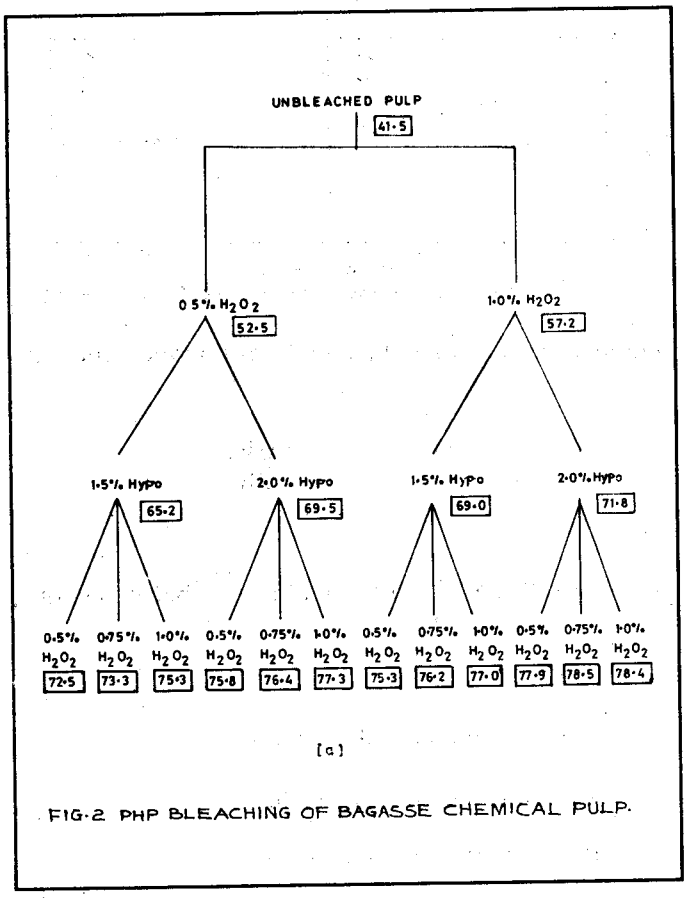
Brightness

The hand sheets were prepared at each of the

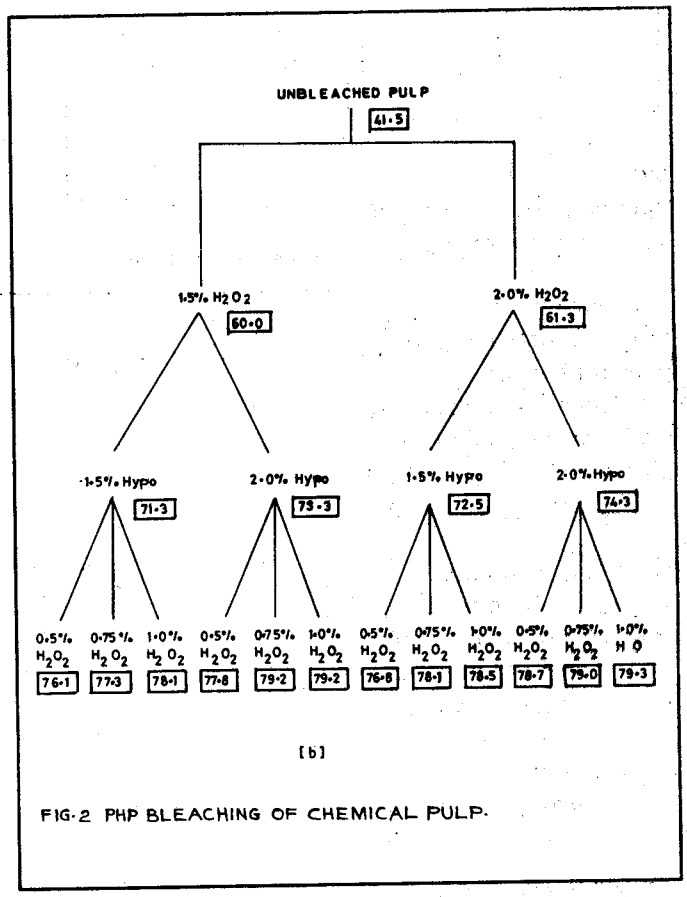
Table-4.

Large Scale Bleaching Experiment

PARAMETERS \ SEQUENCE	CEH			PHP		
	C	E	H	P	H	P
1. Chlorine (AC)% on OD pulp	2.8					
2. NaOH (AC)% on OD pulp		2.0		0.81		0.5
3. H_2O_2 (100%) % on OD pulp				1.0		1.5
4. Ca-Hypo (AC) % on OD pulp			2.5		2.5	
5. Na-Silicate (38 0BE) % on OD pulp				2.0		2.0
6. $MgSO_4.7H_2O$ (AC)% on OD pulp				0.5		0.5
7. Bleaching shrinkage %		6.60			3.60	
8.Tear Factor		24.7			31.3	
9. Burst Factor		38.6			41.4	
10. Breaking length (meters)		2822			3083	



FIG·2 PHP BLEACHING OF BAGASSE CHEMICAL PULP.



FIG·2 PHP BLEACHING OF CHEMICAL PULP.

bleaching stages and the brightness of the same were tested on Technibrite TB 1C instrument. This instrument gives the brightness values directly in ^{0}ISO units.

Post Colour Number (P.C. Number).

The natural aging is very slow and not reproducible. Hence attempts have been made to speed up the aging process by exposure of pulp sheets to higher temperature.

The samples were subjected to 100% humidity at 100^0 C (TAPPI-260) for 1 hour. The brightness values were measured before and after aging and post colour

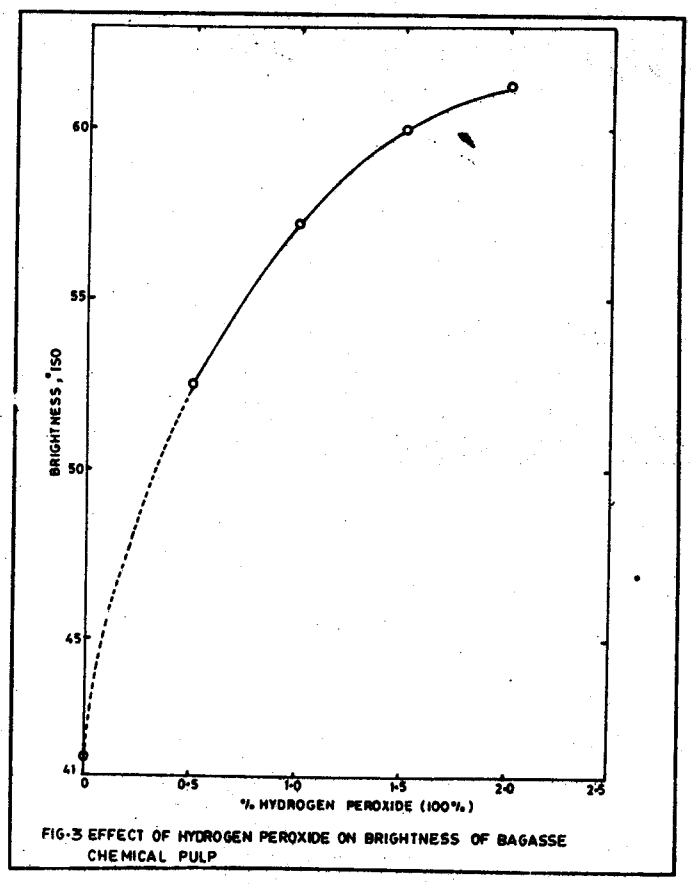


FIG-3 EFFECT OF HYDROGEN PEROXIDE ON BRIGHTNESS OF BAGASSE CHEMICAL PULP

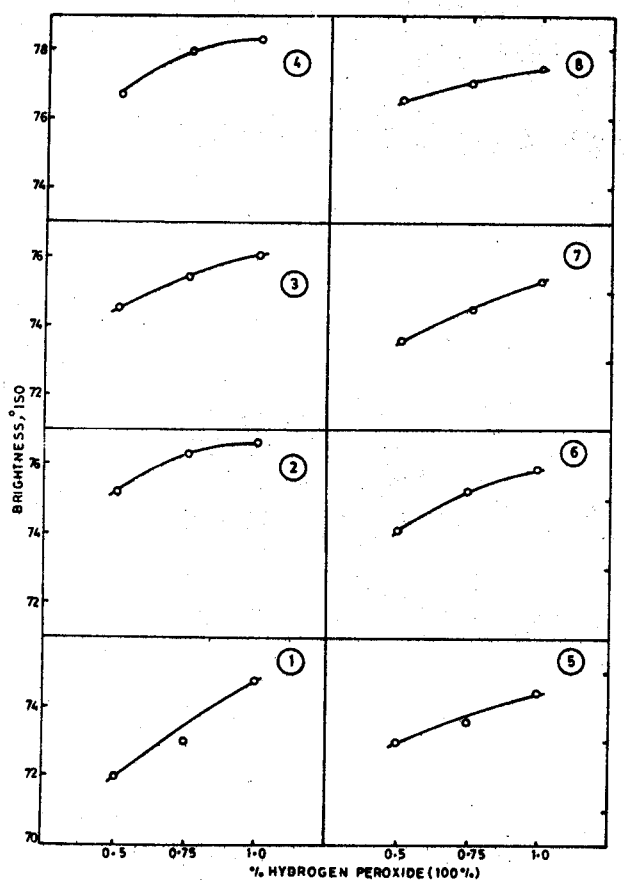


FIG-4 EFFECT OF HYDROGEN PEROXIDE ON PHP BLEACHED BAGASSE CHEMICAL PULP

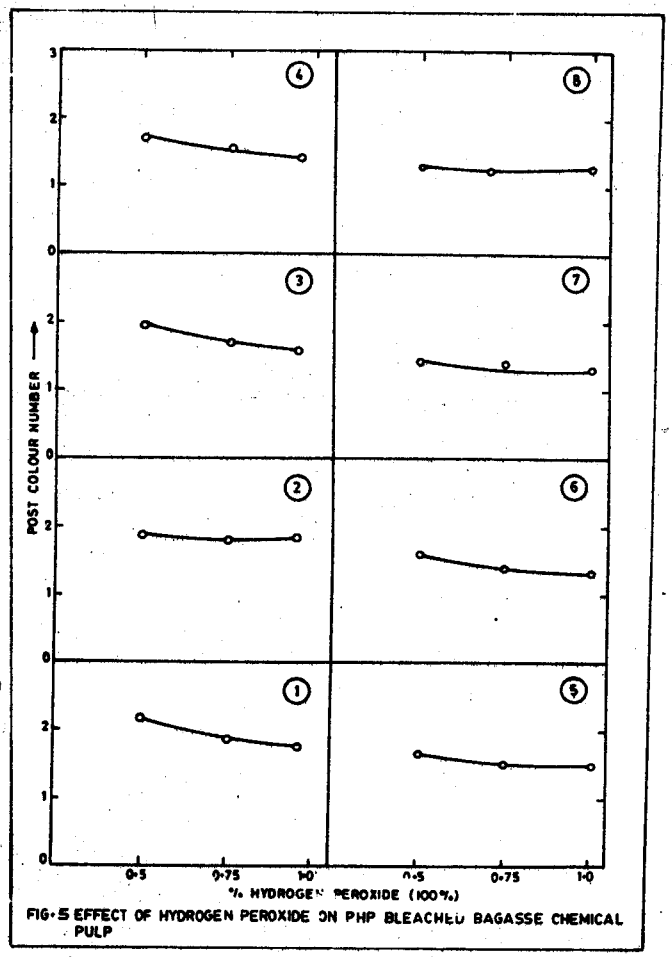


FIG-5 EFFECT OF HYDROGEN PEROXIDE ON PHP BLEACHED BAGASSE CHEMICAL PULP

number was calculated using the following equation.

1.

$$\frac{K}{S} \qquad \frac{(1-R)^2}{2R}$$

2.

$$P.C.No. = 100 \times \left[\frac{(K)}{(S)}\text{after ageing} - \frac{(K)}{(S)}\text{before ageing} \right]$$

where--

K = coefficient of absorption

S = coefficient of scattering

R reflectivity = $\frac{\text{Brightness}}{100}$

CED viscosity values were tested in each set as per TAPPI - 230 procedure.

Mechanical properties such as tear factor, burst factor and breaking length were tested as per TAPPI procedures.

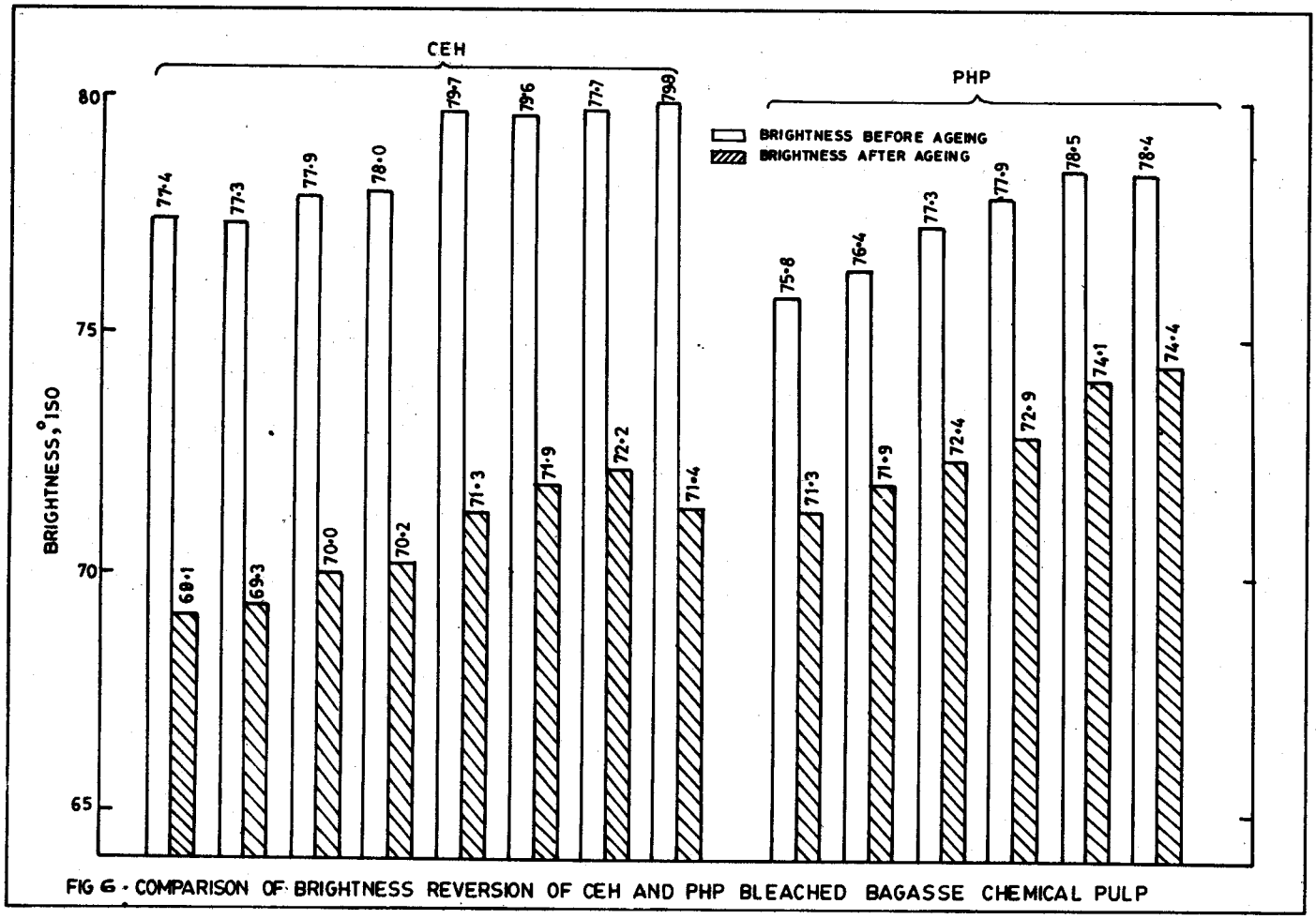


FIG 6 - COMPARISON OF BRIGHTNESS REVERSION OF CEH AND PHP BLEACHED BAGASSE CHEMICAL PULP

RESULTS AND DISCUSSIONS

The unbleached pulp sample under study was having permanganate number (K.No.) of 8.8. On the basis of K.No. the total chlorine demand assumed was 4.4% to 5.2%. This total chlorine was spread over chlorination (C) and hypochlorite (H) stages proportionately during CEH bleaching (Table-2). Hydrogen peroxide concentration were also varied, by restricting hypochlorite concentrations to 1.5 & 2.0% on available chlorine on O.D. pulp (Table-3).

It is well known that brightness of unbleached bagasse chemical pulp increases as hydrogen peroxide concentration is increased. During this study usage of hydrogen peroxide (100%) on unbleached pulp was restricted to 2% on O.D. pulp at first P stage whereas 1% H_2O_2 at second P stage. With 0.5% H_2O_2 (100%) brightness is 52.5 °ISO whereas with 2.0% H_2O_2 (100%) brightness is 61.3 °ISO. This has been shown in Fig. 3 & 4 respectively.

It is observed that when pulp is bleached to almost 80° ISO (79.9 °ISO) in a typical experiment by CED bleaching sequence, its brightness after accelerated ageing goes down to 71.4 °ISO showing reversion in brightness by almost 8.5° ISO units. The same pulp when bleached by PHP sequence the brightness level achieved was 78 °ISO (77.9 °ISO) with 1% & 0.5% H_2O_2 (100%) at first and final stage of bleaching respectively. The brightness after reversion is 72.9 °ISO, i.e. 1.5 units higher than CEH bleached pulp. P.C. no. of PHP bleached pulp is 1.77 as against 3.21 in case of CEH bleached pulp. Similarly Fig. 5 shows that as concentration of hydrogen peroxide at final stage increases the post colour No. (P. C. no.) of pulp decreases. This shows improved brightness stability of pulp with increase in usage of hydrogen peroxide at final stage of bleaching. As against above, whenever pulp is bleached by usage of hypochlorite at the terminal stage of bleaching, no doubt many time pulp brightness is sufficiently high but reversion in brightness is also equally high. This has been shown in Fig. 6.

78 °ISO brightness achieved during CEH bleaching of pulp reverted to 70.2 °ISO whereas 78 °ISO brightness achieved during PHP sequence reverted to 72.9 °ISO during ageing test.

It is also seen from Table 2 & 3 that Cupra Ethylene Diamine (CED) viscosity values for PHP bleached pulp are always on higher side as compared to CEH bleached pulp at same brightness/ reverted brightness level. The improvement in viscosity values indicate that degradation of cellulose in PHP bleaching sequence is less as compared to CEH bleaching of bagasse chemical pulp. Chlorine is not specific in its oxidation reaction and therefore, it attacks cellulose as well as lignin during chlorination (16,17).

Mechanical strength of CEH and PHP bleached pulp when compared (Table-4) was found that PHP bleached pulp was stronger in all respect as compared to CEH bleached pulp. There was 9 % and 7 % improvement in Breaking Length (B. L.) and Burst Factor (B.F.) respectively. The Tear Factor has shown remarkable improvement. This is almost 26 % higher in PHP bleached pulp that CEH bleached pulp. This improvement in mechanical strength may be due to elimination of chlorine totally and reducing hypochlorite partially. The effect of chlorine has been also discussed earlier here in 4.3.

Bleaching shrinkage during large scale PHP and CEH laboratory bleaching experiments were (Table-4) 3.6% and 6.6% respectively. This lower bleaching shrinkage in PHP bleaching could be a combination of improved cellulosic fibres and preservation of modified colourless products of lignin during PHP bleaching.

During this PHP bleaching sequence, almost 50-60% chlorine in the form of elemental chlorine was eliminated. Chlorinated organic were not tested either qualitalively or quantitatively during this study. However, it can be safely assumed, based on literature published (14) that the proportionate reduction in chlorinated organics would be almost by 50% during PHP sequence as compared to CEH bleaching sequence. Thus PHP bleaching would be definitely environmentally friendly as compared to CEH bleaching of bagasse chemical pulp, Earlier it was reported that the reducation in colour of extraction wash liquor of CEpH bleached pulp (4, 5). Similarly here also it was observed that colour of wash liquor at P stages was lighter as compared to extraction wash liquor of CEH bleached pulp.

CONCLUSIONS

Bagasse Chemical Pulp can be bleached by usage of Peroxide - Hypochlorite - Peroxide (PHP) bleaching sequence to acceptable level of brightness.

The brightness stability of PHP bleached pulp is always on higher side as compared to pulp bleaching with CEH bleaching sequence.

It is possible to reduce 50-60% of total chlorine necessary for bleaching during PHP bleaching sequence and thus possible to reduce discharge of organically bound chlorine in effluent/ pulp and paper.

The mechanical properties of PHP bleached bagasse chemical pulp are better than CEH bleached bagasse chemical pulp.

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