

Conversion from C-E-H-H sequence to C-E-H-H-P sequence to bleach kraft chemical pulp in the Sirpur Paper Mills Limited—a technology updating

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INTRODUCTION :

Peroxide has been and is being used to bleach chemical pulps (both sulphite and kraft) in variety of ways. When used in an intermediate stage, say a P-stage or during alkali extraction (EPO stage), the purpose is primarily to delignify, though brightness increase may be significant. When applied in the final stage, the dominant action is oxidative and aimed at imparting a high and stable brightness. The brightness gain derived from peroxide varies considerably, depending upon the circumstances of application. When used in the last stage of bleaching sequence, incremental improvements are greatest in the semibleached range but peroxide contributes significantly to the brightness of pulp even in the superbleach category. Brightness stability is a major attribute of the bleached pulps provided the peroxide comprises the final stage of the bleaching process (1).

Before the widespread adoption of chlorine dioxide, peroxide was used in combination with hypochlorite in sequences, of the type CEHEHP or CEHPHP (2). Peroxide was more suitable in short sequences of the type CEHP for producing brightness values in the range of 75–85.

Back ground :

From the work carried out in our R & D department and also from the work carried out for our pulp in the laboratory of M/s National Peroxide Limited, (3). We found that CEHH bleached pulp when further bleached by a P-stage (0.5% H_2O_2), the brightness increase of 2-5 °GE units could be achieved in addition to improved brightness stability.

A decision was taken to modify our old bleach section to bleach part of the CEHH bleached pulp (20-25 t/d) by additional one peroxide stage.

The modifications were carried out. The necessary modifications were minimum as we have full stream to bleach 20–25 t/d pulp in our old bleach section. The modifications were (i) Installation of heater-mixer to feed the pulp to T_4 (ii) Necessary treatment to T_4 (iii) storage, dilution and feeding arrangements for sodium silicate, Magnesium sulphate and hydrogen peroxide. Flow diagrams are given in Fig. 1 & 2 for old pulp section (OPS) and new pulp section (NPS) respectively.

Plant Trials :

1st plant trials were carried out from 27th November, 1991 to 30th December, 1991. During these trials, process was controlled at the required level by regular measurement of the concentrations and flows of the chemicals and process parameters such as consistency, pH and temperature. The dosage of chemicals was as given below on O.D. pulp basis.

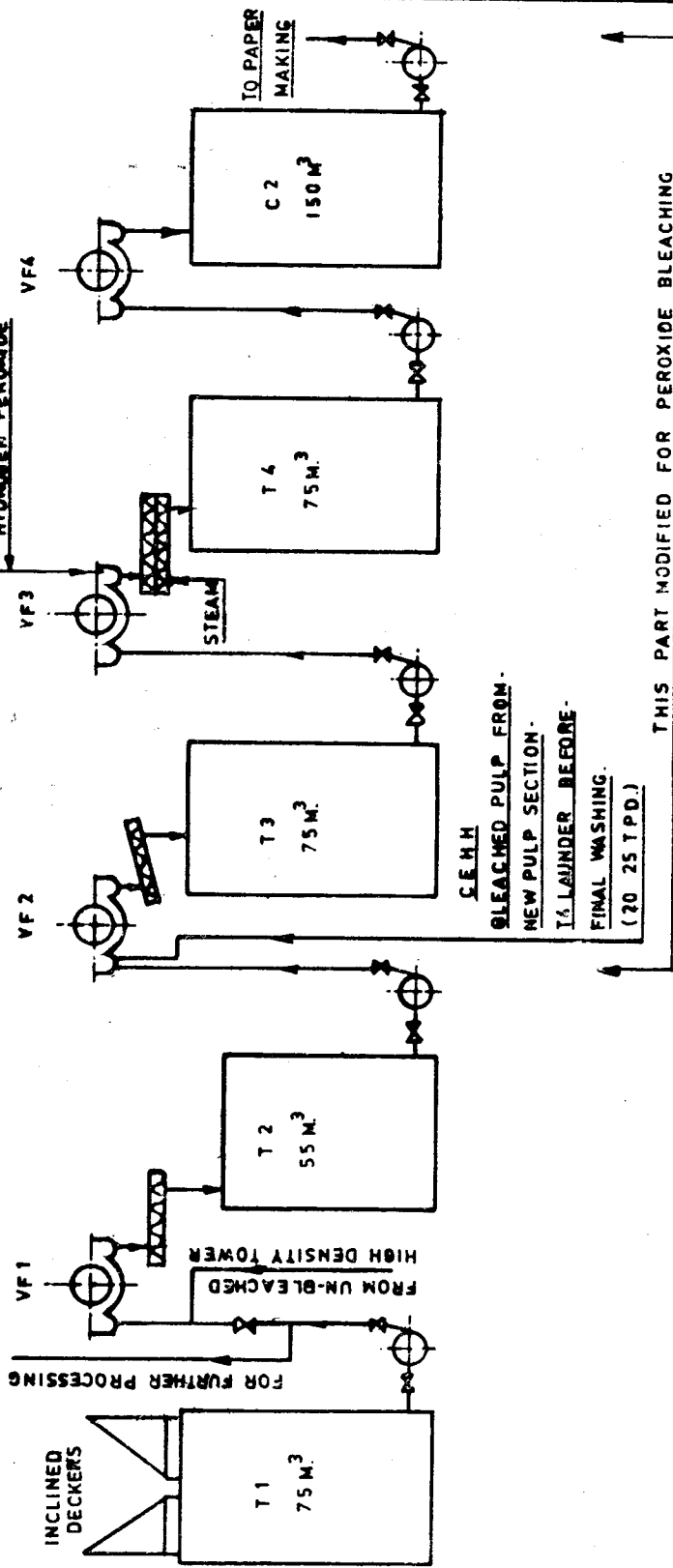
Hydrogen peroxide, on as received basis	1.0% & 1.5%
on 100% basis	0.5% 0.75%
Sodium silicate (53 °Be)	0.7%
Magnesium sulphate hepta hydrate	0.05%
Caustic soda	0.8%

The reaction parameters were controlled as given below :

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Sirpur-Kaghnagar-504 296 (A.P.)

FIGURE-1



REV. NO.	DATE	DRN	CHD	APPD.	REVISIONS

THE SIRPUR PAPER MILLS LTD
SIRPUR-KACHAZNAGAR (A. P.)

Old Pulp Section (O.P.S.) Flow Diagram

DRNG S. No.	S. ON	SCALE	%
TRD	16.06.1993	C. ON	
CHD	A. PD	DRG No	4-3600515

T1 TO T4 REACTION TOWERS
VF1 TO VF4 VACUUM FILTERS
C2 CHEST No. 2

Consistency	7 to 8.5%
Initial pH	10.5 - 10.7
Temperature	60 - 65 °C
Retention time	3-4 hours

The average results obtained during these trials are given in Table-I

TABLE—I

Brightness and P. C. Number before and after H₂O₂ bleaching
(Average of hourly or 2 hourly data averaged for each shift for each day)

Date	OVF ₃ Pulp Pulp before H ₂ O ₂ bleaching		OVF ₄ Pulp Pulp after H ₂ O ₂ bleaching		Difference	
	Brightness °GE	P. C. Number	Brightness °GE	P. C. Number	Brightness °GE	P. C. Number
					(INCREASE)	(DECREASE)
27-11-91	77.15	14.80	77.31	6.28	0.16	8.54
	76.70	16.20	78.75	5.04	2.05	11.16
28-11-91	78.80	14.86	79.25	3.48	0.45	11.38
	77.40	18.55	77.25	6.04	-0.15	12.51
	76.25	17.00	78.37	5.60	2.12	11.4
29-11-91 (0.75% H ₂ O ₂)	75.60	16.70	79.56	5.96	3.96	10.24
	79.62	15.58	81.00	5.56	1.38	10.02
	76.62	23.80	78.00	4.92	1.38	18.88
30-11-91	76.31	17.71	79.56	5.49	3.25	12.22
	80.56	16.66	81.50	7.37	0.94	9.29
	77.50	19.10	78.87	6.40	1.37	12.7
01-12-91	76.56	16.04	79.43	7.59	2.87	8.45
	78.31	14.15	78.50	6.06	0.19	8.09
Grand Avg. 0.5% H ₂ O ₂ Period	77.55	16.51	78.14	5.93	0.59	10.58
0.75% H ₂ O ₂ period	77.3	18.70	79.70	5.48	2.4	13.22

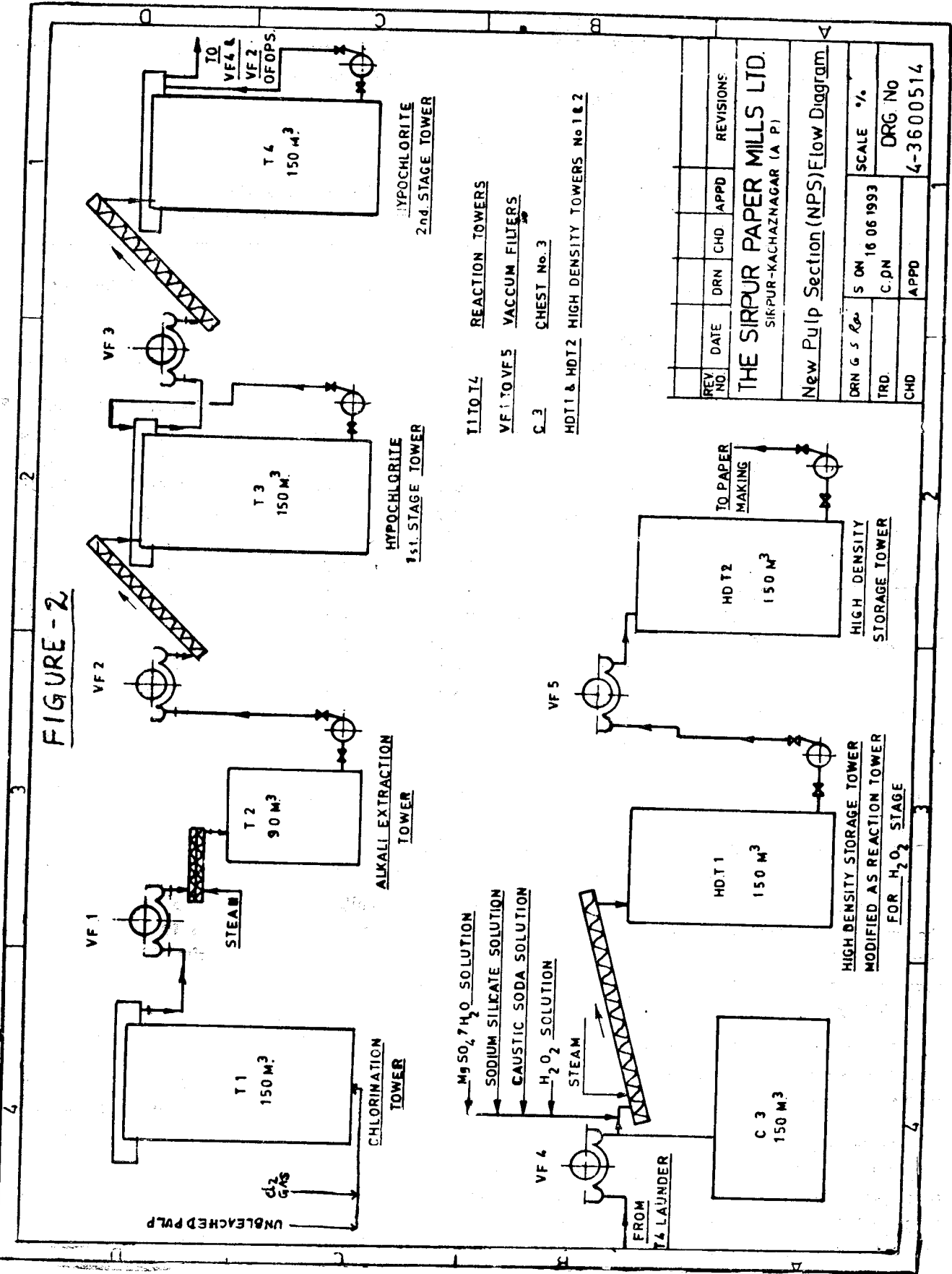
From this trials, it was found that, on an average, the brightness increase achieved at 0.5% H₂O₂ addition level was 0.59 units for the total period. If we compare values on shift-wise basis, the increase has been nil to 3.96 units.

With respect to P. C. Number, the overall reduction has been 10.58 units and shift-wise basis it was 8.09 to 18.88 units.

During this trial, the H₂O₂ dosing was increased from 0.5% to 0.75% (period 20 hours) and the results indicated more improvement as compared to 0.5% H₂O₂ period. Here, the average increase in brightness was 2.4 units and P.C. No. reduction was 13.22.

While plant trials were going on, we carried out a few laboratory experiments to get more insight into the process. In the 1st series of experiments, the effect on the final pulp with and without H₂O₂ addition but with all other additives was studied. The data are given in Table II. From these results, it is clear that when H₂O₂ is excluded, the brightness has fallen from initial 77.5 °GE to 67.5 °GE where as at 0.5% H₂O₂ addition the brightness has increased from 77.5 °GE to 81.5 °GE. In both the cases the P.C. Number reduction is substantial as expected. This experiments confirmed the earlier data that it is the higher pH and temperature which are responsible for P. C. Number reduction and the function of

FIGURE-2



REV. NO.	DATE	DRN	CHD	APPD	REVISIONS

THE SIRPUR PAPER MILLS LTD.
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New Pulp Section (NPS) Flow Diagram

DRN G S R	S ON	16 06 1993	SCALE	%
TRD.	C.P.N		DRG No	
CHD	APPD		4-3600514	

TABLE-II

CEHH bleached pulp further bleached with hydrogen peroxide.
 Expt 1 : without H₂O₂ but with other chemicals,
 Expt 2 : All chemicals + H₂O₂
 Initial Pulp : Brightness 77.5°C
 P C. Number 17.5

Experiment No.	1		2		3
	Without H ₂ O ₂ (a)	(b)	With H ₂ O ₂ (a)	(b)	
	Plant pulp after dosing all chemicals before entering reaction tower but was retained in Lab. water bath				
Dosage of chemicals (on O. D. pulp basis)					
Mg SO ₄ . 7H ₂ O	0.05	0.05	0.05	0.05	0.05
Sodium Silicate	1.0	1.0	1.0	1.0	1.0
Caustic Soda	0.8	0.8	0.8	0.8	0.8
H ₂ O ₂ , %	Nil	Nil	0.5	0.5	0.5
PH : Initial	10.9	11.0	10.6	10.6	10.6
Final	9.1	9.1	8.7	8.6	8.5
Temperature, °C	-----65±2°C-----				
Retention time, hr.	-----3-----				
Brightness, °GE	67.5	67.5	81.5	81.5	78.5
P. C. Number	3.1	3.8	3.8	4.1	5.7

H₂O₂ is to destroy the colouring matter so generated (1). From these experiments, it is important to note that, during plant operation H₂O₂ addition is stopped for some time for any reason or the system is contaminated with metal ions (iron, copper, chromium, vanadium, tungsten, molybdenum, silver) which decompose hydrogen peroxide before they have chance to react with colouring matter generated, the resulting pulp would be of substantially lower brightness than the feed pulp. This pitfall has to be guarded against during plant operation, on two occasions we faced such a problem.

Strength Properties of Pulp :

During the above trials, we collected composite samples (composited over 48 hours) of bleached pulp before and after hydrogen peroxide bleaching. These pulps were evaluated for strength properties by beating in laboratory beater and making standard hand sheets. The data are given in Table-III. It is observed that there is no significant change in strength properties.

TABLE-III

Strength properties of pulp before & after H₂O₂ stage

	Before H ₂ O ₂	After H ₂ O ₂
Initial Freeness, °SR	15	16
Beating Time, min.	45	42
Grammage, g/m ²	62	61
Caliper, μm	80	80
Bulk, Cm ³ /g	1.29	1.31
Tear Factor	49.4	50.3
Burst Factor	41.3	37.0
Double Folds (Kohler Molin)	114	100
Strength Index*	1614	1550
Unbeaten Pulp :		
Brightness of pulp	73.5	75.5
P. C. Number	14.0	4.6
0.5% CED viscosity at 20°C, mPa.s	7.3	7.2

* (Burst Factor x Tear Factor x Log₁₀ Double folds)^{1/3} x 100

T A B L E - IV

Aging properties of Duplex Board Topliner Comparison of CEHH and CEHHP bleached pulp used as topline (Sample of March, 1992)

Sequence Ageing procedure	CEHH					CEHHP					CEHH			CEHHP		
	Hung in oven at 105 ± 2°C for 24 hours										Exposed to Sunlight for 2 hours (between 9 00 and 11 00 AM)					
	1	2	3	4	5	1	2	3	4	5	1	2	3	1	2	3
Brightness °GE																
Before ageing	73.5	73.0	73.0	73.0	73.0	74.0	75.0	74.0	72.5	73.0	73.5	73.0	73.0	74.0	75.0	75.5
After ageing	59.5	55.0	55.0	61.0	58.5	63.0	65.0	65.5	54.0	63.0	66.0	65.5	65.5	70.0	70.0	69.5
Difference (loss of brightness points)	14.0	18.0	18.0	12.0	14.5	11.0	10.0	8.5	8.5	10.0	7.5	7.5	7.5	4.0	5.0	6.0

Regular Production of C-E-H-H-P Pulp :

From the foregoing it can be seen that a last stage peroxide bleaching improves brightness and brightness stability. After attending to problems observed during these trials, regular production was started from March, 1992. We have found that there is significant improvement in quality of paper and or Duplex board manufactured using this pulp.

Ageing properties of Duplex board manufactured with C-E-H-H and C-E-H-H-P pulp are given in Table-IV. These data clearly indicate the quality improvement with respect to brightness stability.

Table-V gives data of the pulp bleached by C-E-H-H-P sequence in the laboratory and plant. Brightness as tested on 28-11-1991 and the brightness data tested on 12-6-93 (after 1½ years) are also given. These data,

confirm the brightness stability achieved. Recent data regarding brightness and P. C. Number are given in Table-VI.

TABLE-V

Data as on	Before H ₂ O ₂ bleaching	With all chemical additives except H ₂ O ₂	After H ₂ O ₂ bleaching	
			Lab	Plant
28-11-1991				
Brightness, °GE	77.0	68.5	82.0	78.0
P. C. Number	17.5	3.8	4.0	5.7
Data as on				
12-6-1993				
Brightness, °GE	62.0	69.0	76.5	74.0

TABLE-VI

Average pulp properties day-wise before and after peroxide bleaching (recent data) two hourly data averaged)

Date	CEHH Pulp		CEHHP Pulp		Difference	
	Average Brightness °GE	Average P. C. Number	Average Brightness °GE	Average P. C. Number	Brightness (Increase)	P. C. Number (Decrease)
08-06-93	77.9	10.4	78.8	5.85	0.9	4.55
10-06-93	77.2	14.8	80.3	3.75	3.1	11.05
11-06-93	76.1	12.8	79.3	4.76	3.2	8.34
12-06-93	77.9	9.9	79.8	5.09	1.9	4.81
13-06-93	78.6	14.2	78.8	3.55	0.2	10.65
14-06-93	75.8	13.8	76.8	5.86	1.0	7.94
15-06-93	78.3	9.7	78.8	3.57	0.5	6.13

Cost of Bleaching :

The additional operating cost for one stage peroxide with 0.5% H₂O₂ dosage has worked out to around Rs. 400/- per tonne.

Future Plan :

Because of the success achieved in improving pulp quality by C-E-H-H-P bleaching, we have now modified our plant for bleaching total pulp (100 t/d) by

this sequence and the trials have given, similar results obtained earlier in the modified old pulp section (20-25 t/d). We intend using this pulp for value added products.

References :

- (1) Singh, R.P., Ed., The bleaching of Pulp, 3rd edition, (1979) Tappi Press.
- (2) Miller R.L., et al, Tappi 39 (11) : 826-829 (1956)
- (3) Private communications from M/s National Peroxide Limited.