Bleaching of Kraft Pulp by Multistage Conventional (C-E-H-H) Sequence After 1st Oxygen Stage

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ABSTRACT: *Kraft pulp (65% Bamboo and 35% mixed Hardwood furnish) of 23-29 Kappa Number has been bleached under different conditions in 1st oxygen stage to optimize the variables taking into consideration the existing conditions in the mills. These experiments indicate that such a pulp can be bleached to reduce Kappa Number by 40 - 45% under the conditions namely 2.5% NaOH charge, 97± 2°C temperature, 1 h retention time, 8% consistency and 4 to 5 Kg/Cm² (400 to 500 K Pa) oxygen pressure. The loss of viscosity after oxygen stage is quite low. Such a pulp when further bleached by C-E-H-H sequence (i.e. O-C-E-H-H) is comparable in strength levels and yield loss to straight C-E-H-H sequence. However, for O-C-E-H-H pulp the total available chlorine required to bleach to 80% brightness is substantially lower thereby reducing chlorine consumption. As the 1st oxygen stage liquor can be recirculated to recovery system, the reduction in colour, BOD, COD and dioxins would be substantial.*

INTRODUCTION

In India, the generally used multistage bleaching sequence is C-E-H-H in most of the integrated pulp and paper mills. Of late, some mills have introduced Chlorine Dioxide stage also and use such sequences as C-E-H-D-E-D or the standard C-E-D-E-D. Infact C-E-D-E-D sequence has been the industry's standard sequence in developed countries for many years (1). However, with increased knowledge about the formation of toxic dioxins and furans in chlorination stage, there has been lot of changes to reduce or eliminate the formation of these compounds (These are measured in pulp or effluent as AOX or Tocl). One important modification is to replace chlorine in the chlorination stage by chlorine dioxide partly or wholly. Other routes followed in developed countries are extended

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delignification before bleaching (i.e. cooking to lower Kappa Numbers) or oxygen bleaching. However, in India, use of molecular oxygen for bleaching pulps have been introduced only recently in a few mills, that too in alkali extraction stage. In the alkali extraction stage, the additional drop in Kappa Number expected in only 2 to 3 units by EO treatment as compared to E treatment. This is quite beneficial in reducing pollution load (colour, BOD & COD) and also to reduce hypochlorite and chlorine dioxide demand in subsequent stages to some extent.

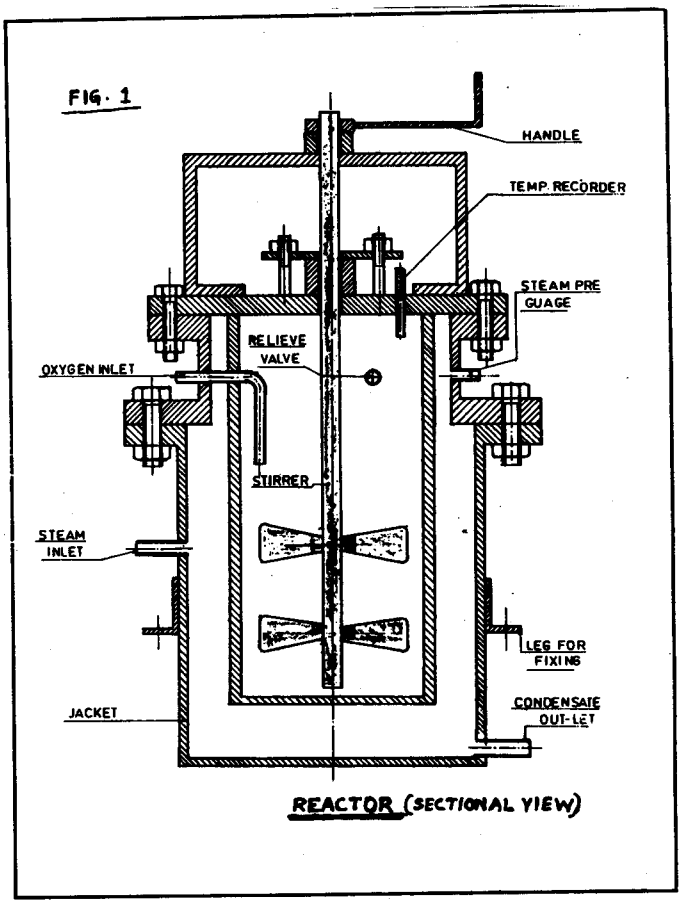
However, if molecular oxygen bleaching is carried out as a 1st stage, the Kappa Number reduction would be substantial. It is found that it should not be extended beyond 40 to 50% reduction to prevent pulp degradation and yield loss even in the presence of Magnesium Compound inhibitors (2) Recent work indicates that the efficiency of oxygen stage can be improved by pretreatments such as nitrosation or Sodium Nitrite treatment (3) and prenox (4). As a corollary, the pollution load and total chlorine demand for further bleaching would also get reduced substantially.

Infact Environmental protection Agency of USA has issued in November, 93 a proposed series of regulations to Clean Air Act and the clean water Act that will necessitate use of Best Available Technology (BAT) to reduce Colour & Toxins. The Best Available Technology is either extended delignification or oxygen delignification and ClO_2 bleaching (5).

This paper deals with Kraft pulp bleaching by O-C-E-H-H sequence in comparison with C-E-H-H. The pulps used for these studies were Kraft chemical pulps from plant with approximate furnish composition of 65% bamboo and 35% mixed hardwoods.

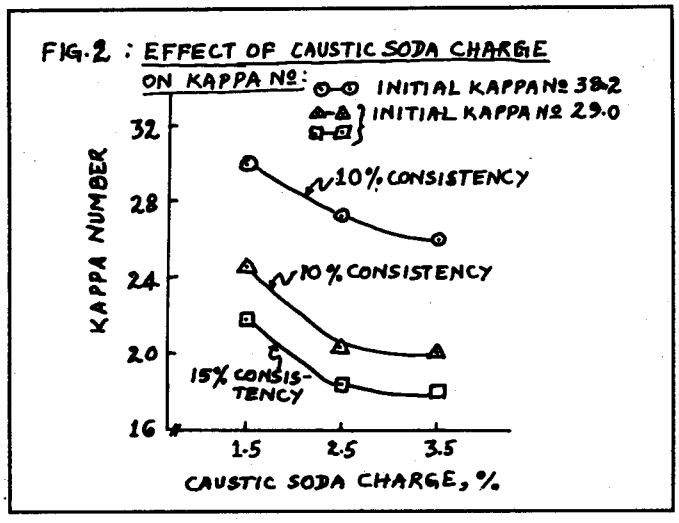
EXPERIMENTAL

Oxygen bleaching experiments were carried out on unbleached pulp batches equivalent to 100 g O.D. using a stainless steel reactor with steam jacket for raising the temperature to the desired level. The reactor is also equipped with a mixer to be operated manually as and when required



(Please see Fig. 1 showing a sectional view of the reactor).

After thickening the screened unbleached pulp from plant to the required consistency, the pulp was charged to the reactor. Required amount of caustic soda and magnesium sulphate were added to the pulp and then mixed well after addition of each. After this, the lid of the reactor was closed and the temperature was raised to the required level by steaming indirectly. After attaining reaction temperature, oxygen from oxygen cylinder was fed and required pressure was maintained throughout the reaction time by controlling oxygen inlet valve. The temperature of reaction was also maintained at the required level by steam control to the jacket. During the reaction period, the pulp was mixed every 5 minutes by operating the mixer. After completion of reaction time, steam supply and oxygen supply were cut off, the pressure was released and the pulp was taken out and washed for further processing. Further bleaching by C-E-H-H was carried out on the oxygen bleached pulps.



RESULTS & DISCUSSION

From Fig. 2 and Table-I it is seen that, for the type of pulp bleached, 2.5% caustic soda is sufficient as higher dosage has not indicated corresponding Kappa Number drop. This is applicable both for higher Kappa Number pulp (38.2) and medium Kappa Number pulp (29.0). It is also observed that higher consistency of 15% is better than 10% consistency. However, this will not be practicable in view of the limitation of equipment.

Table-1

Effect of caustic soda charge and two consistency levels in the 1st Oxygen stage on Kappa Number

Set No.		1			2			3	
Initial Kappa No.		38.2			29.0			29.0	
Expt. No.	1	2	3	4	5	6	7	8	9
Caustic Soda Charge (% on O.D. unbld. pulp)	1.5	2.5	3.5	1.5	2.5	3.5	1.5	2.5	3.5
Consistency %	10	10	10	10	10	10	15	15	15
Final Kappa No.	30.2	27.4	26.1	24.6	20.4	20.2	21.8	18.4	18.2

Constant Conditions:		
	Reaction temperature	97 ± 2°C
	Retention time	45 minutes
	Oxygen Pressure	4.0 Kg/cm²
	$MgSO_4 . 7 H_2O$% (on O.D. pulp basis)	0.5%

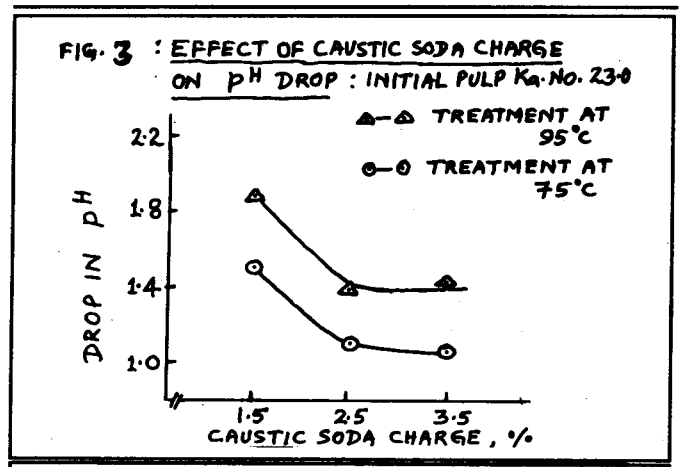
Further studies of the effect of alkali charge with an initial Kappa Number pulp of 23.0 are given in Table-II and Fig. 3 and Fig. 4. From Fig. 3 it is seen that the rate of pH drop reduces considerably after 2.5% caustic soda charge indicating that its effectiveness also drops (both at 75°C & 95°C). Similar trend is observed on Kappa Number reduction but higher temperature is found to be more effective (See Fig. 4).

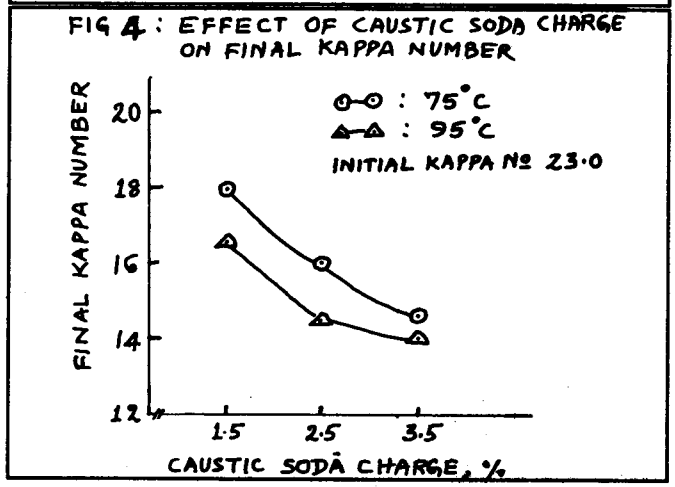
Table-2

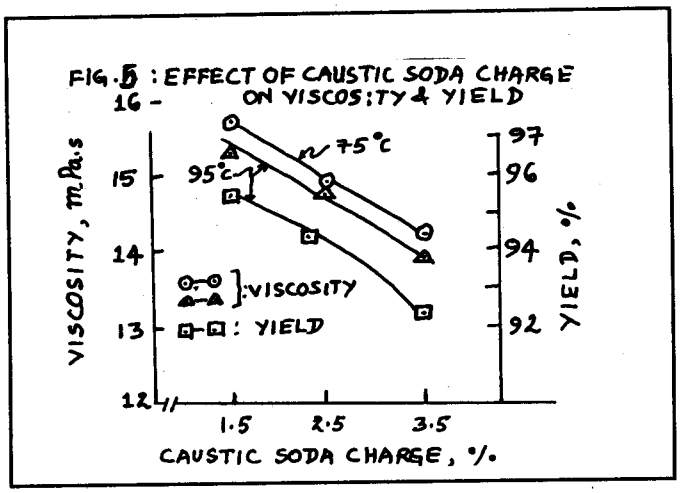
Effect of caustic soda charge at two temperature levels

Initial pulp Kappa Number	23.0					
Viscosity (0.5% CED)	16.5 m Pa. s					
Set No.		A			B	
Temperature of Reaction,°C		75			95	
Oxygen Pressure Kg/cm²		4.0			4.0	
Expt. No.	1	2	3	1	2	3
Caustic Soda Charge % (on O.D. pulp basis)	1.5	2.5	3.5	1.5	2.5	3.5
Initial pH	11.98	12.51	12.81	11.91	12.57	12.85
Final pH	10.48	11.41	11.74	10.14	11.19	11.42
Final Pulp Kappa No.	18.0	16.0	14.6	16.6	14.5	14.0
Final pulp Viscosity m Pa.s	15.7	14.9	14.2	15.3	14.8	14.0
Pulp yield % (O.D. initial pulp basis)	--	--	--	95.5	94.5	92.3

Constant Parameters:		
	Retention time	1 h
	Consistency	8 %
	$MgSO_4 . 7 H_2O$	0.5 %







As the caustic soda charge is increased, the viscosity of the resulting pulp drops both at lower temperature (75°C) and at higher temperature (95°C) and the drop is higher at higher temperature. Also as the alkali charge increases, the final pulp yield decreases indicating degradation and depolymerization of cellulose. Hence it is necessary that the alkali charge is not excessive (Please see Fig. 5 & Table-II).

Table-3

Effect of further bleaching by C-E-H-H sequence.

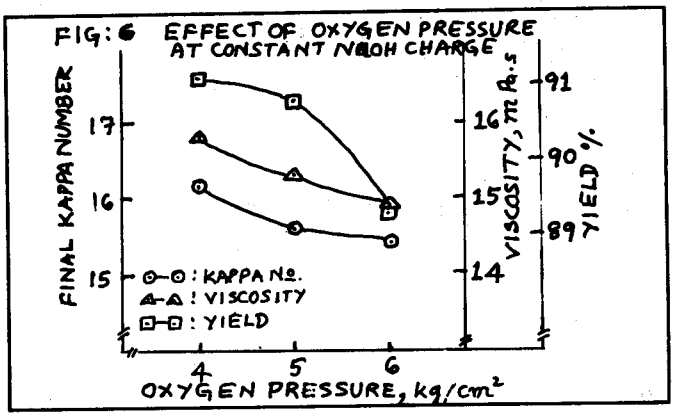
Oxygen bleached pulps bleached using three levels of Caustic soda charge (Set 'B' of Table-2)

Expt. No.	1	2	3
Caustic Soda Charge used for oxygen stage %	1.5	2.5	3.5
Total chlorine consumed for CEHH bleaching%	1.67	1.37	1.34
Final bleached pulp yield on O.D. unbld. pulp basis, %	90.7	90.2	88.5
Final bleached pulp properties			
(a) Brightness, °GE	79.0	78.5	78.0
(b) P.C. number	9.1	9.0	8.8
(c) Viscosity, m Pa.s (0.5% CED)	7.24	7.04	6.76

C-E-H-H bleaching condition

	Consis-tency	Retention time. h	Tempera-ture °C	Sulphamic Acid, %
Chlorination stage	3.0	1	Ambient	--
Alkali extraction stage	7.0	3/4	67	1.5 (Caustic soda)
Hypochlorite - I stage	7.0	2½	37	0.1
Hypochlorite - II stage	7.0	2	37	--

Note: Consistency in alkali extraction and hypochlorite stages was kept at 7% considering our plant capacity.



From Fig. 6 and Table-IV, it can be seen that, though higher oxygen pressures are beneficial in increasing delignification to some extent, it has adverse effect on yield and viscosity and unduly high pressure should be avoided, especially if the mixing is improper.

Table-4

Effect of oxygen pressure at constant caustic soda charge

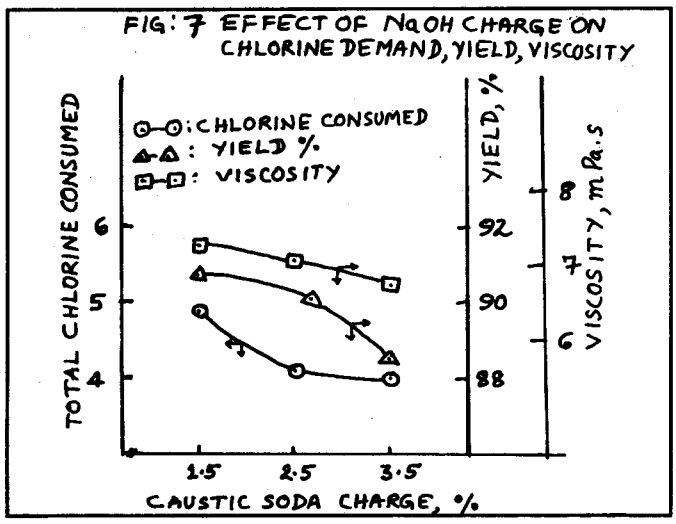
Initial pulp Kappa Number: 26.5, Viscosity (0.5% CED): 17.2 mPa.s

Expt. No.	1	2	3
Caustic Soda Charge on O.D. pulp basis, %	2.5	2.5	2.5
Oxygen Pressure, Kg/cm²	4.0	5.0	6.0
Initial pH	12.14	12.21	12.31
Final pH	10.53	10.36	10.28
Final pulp Kappa No.	16.2	15.6	15.4
Final pulp Viscosity, mPa.s	15.8	15.3	14.9
Final pulp yield on O.D. initial pulp basis, %	91.1	90.8	89.3

Constant parameters:		
	Caustic Soda charge	2.5%
	Reaction tamperature	95 ± 2°C
	$MgSO_4 . 7 H_2O$, %	0.5
	Retention time	1.0 h

As the effect of caustic soda charge is to decrease the Kappa Number, the pulps bleached with higher caustic soda charge consume less chlorine but the final pulp yield (Bleached) and the viscosity of the bleached pulp are lower for pulps bleached with higher caustic soda charge (Please see table-III and Fig. 7).

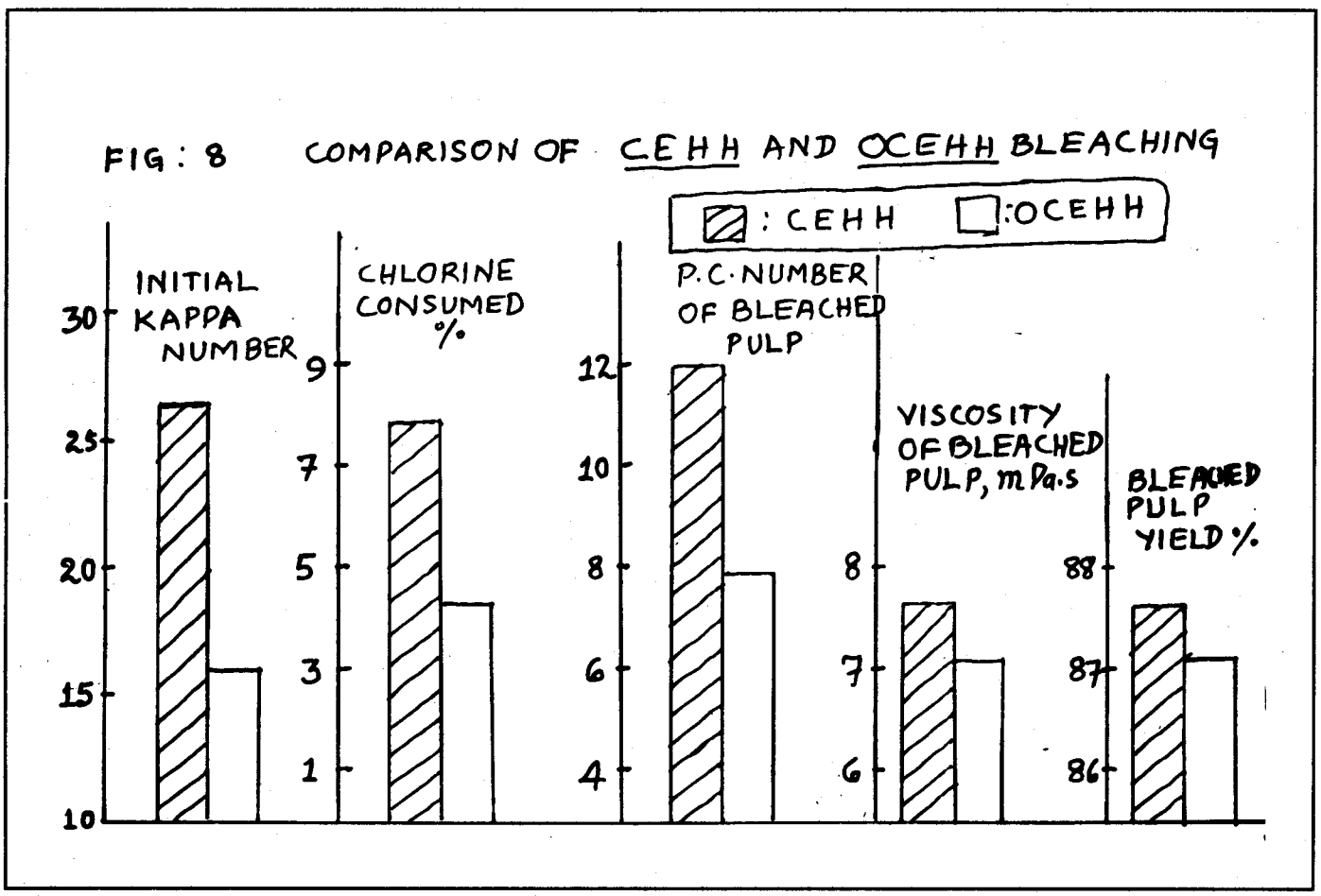
From the above it is seen that the optimum conditions for the type of pulp used, are (i) caustic soda charge 2.5% (ii) temperature 95°C (iii) oxygen pressure of 5 Kg/cm² (iv)Consistency 10%, and (v)



Retention time 1 hour.

Though the effect of time has not been studied, literature survey indicates that 45 minutes to 1 hour are optimum for most of the pulps. Hence 1 hour has been considered for further work. Though some work has been done by others with respect to the effect of magnesium compounds, this was not considered for our study as it has been found by most of the work that their presence is beneficial as a free radical scavengers and as such, 0.5% $MgSO_4 . 7 H_2O$ was used in all experiments. Consistency was maintained at 8% in view of the thickening capacity of our mills. (These experiments have been carried out with a view to incorporate 1st oxygen stage in our mills.)

With these optimum conditions, about 500 g of unbleached pulp (of kappa number 26.5) was bleached by 1st oxygen stage and then by C-E-H-H sequence. Unbleached pulp was also bleached seperately by C-E-H-H sequence for comparison. Please see Table-V and Fig.8 for comparison of pulp data and Table-VI & Fig.9, for strength properties of the pulps. From Fig.8, it is clear that for O-C-E-H-H sequence, the chlorine requirement has reduced significantly as compared to C-E-H-H sequence. Also the P.C. number of O-C-E-H-H pulp is significantly lower indicating



better brightness stability.

Table-5

Bleaching of unbleached pulp and Oxygen bleached pulp by CEHH sequence

Initial pulp	Unbleached pulp	Oxygen bleached Pulp
Kappa number	26.5	16.0
Total chlorine consumed,%	7.90	4.33
Final pulp properties		
(a) Brightness °GE	81.0	80.0
(b) P.C. Number	11.97	7.86
(c) Viscosity, mPa.s	7.64	7.11
(d) Pulp yield, %	89.6	89.1

Bleaching Conditions

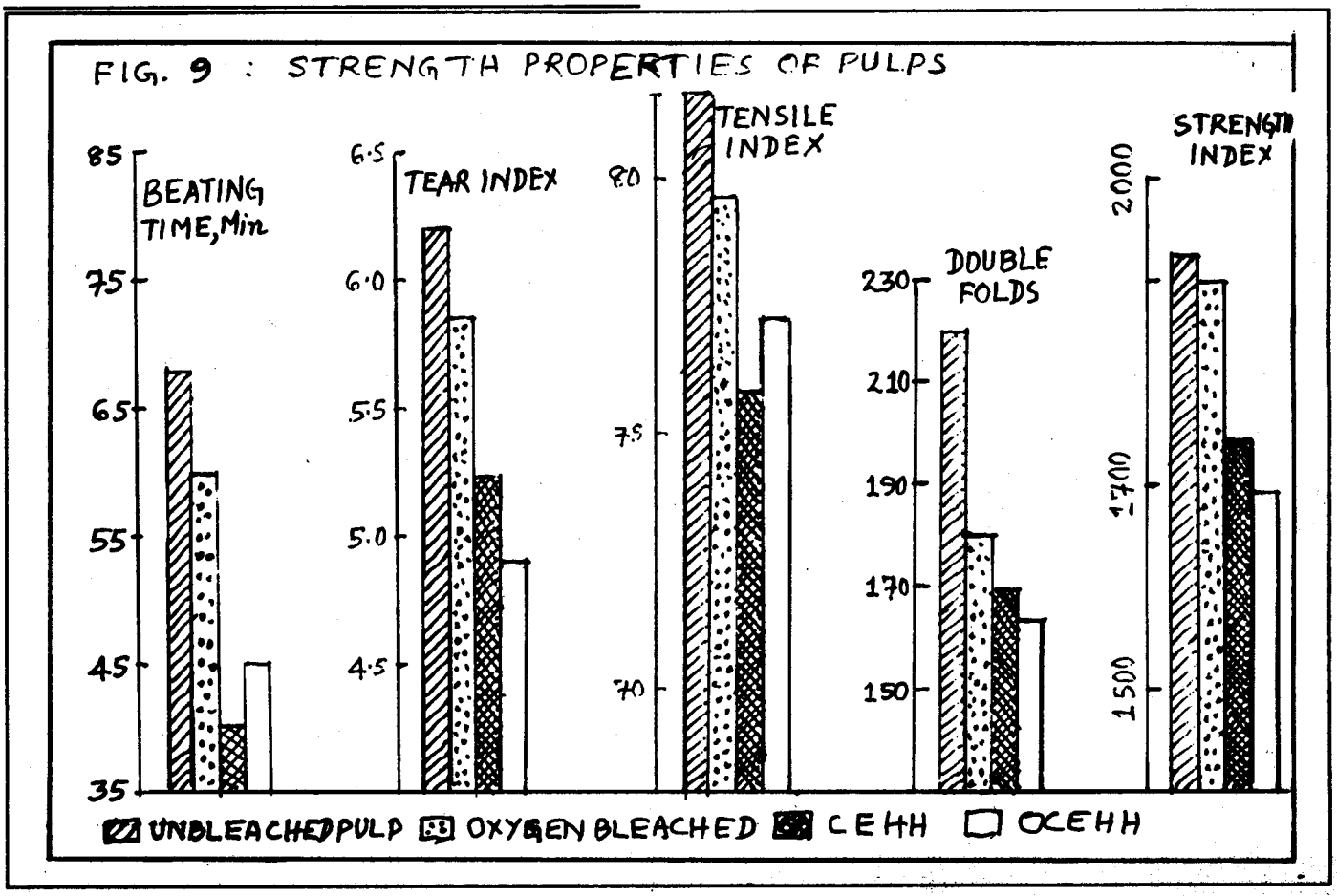
	Temp. °C	Retention time, h	Pressure, Kg/cm²	Consis-tency, %	% Chemical Addition
1st Oxygen stage	97±2	1	5	8	2.5% NaOH & 0.5%$MgSO_4.7H_2O$
Chlorination stage	Ambient	1	Ambient	3	--
Caustic Ext-raction Stage	65±2	3/4	"	7	1.5% NaOH
Hypochlorite 1st stage	37±2 Acid	2½	"	7	0.1% Sulphamic
Hypochlorite 2nd stage	37±2	2	"	7	--

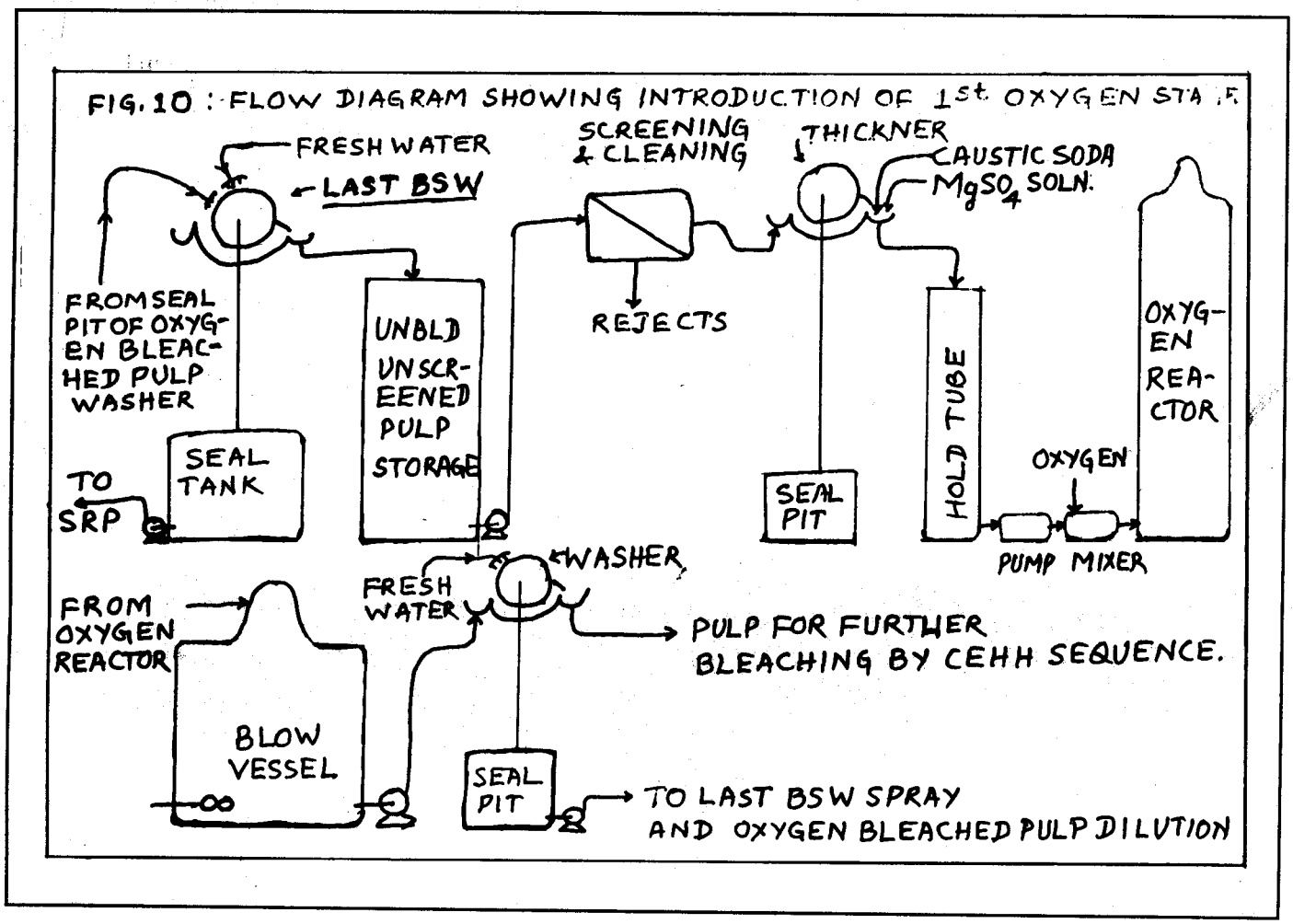
Table-6

Strength properties of pulps

	Unbld. pulp	Oxygen bld. pulp	CEHH bld. pulp	OCEHH bld. pulp
Initial Freeness, °SR	18	16	15	15
Final Freeness, °SR	41	40	40	41
Beating time, min.	68	60	40	45
Grammage, g/m²	63	62	62	60
Caliper, Um	100	95	90	90
Bulk, Cm³/g	1.58	1.53	1.45	1.50
Tear Indes, mN.m²/g	6.22	5.85	5.21	4.90
Burst Index, KPa.m²/g	4.70	5.00	4.37	4.49
Tensile Index, N.m/g	81.74	79.63	75.75	77.34
Folding Endurance, No. of D.F.'s (Kohler Molin)	220	180	170	164
Strength Index	1925	1900	1743	1692

From Fig.9 and Table VI, it is seen that the oxygen bleached pulp is slightly weaker than unbleached





pulp which is expected and that O-C-E-H-H bleached pulp is almost comparable to C-E-H-H bleached pulp.

The schematic flow sheet for incorporating 1st oxygen stage in the existing mills using C-E-H-H sequence is given in Fig.10. It should be noted that the washing after oxygen stage has to be thorough to minimize chemical consumption in the succeeding stages of bleaching to ensure that full advantage of oxygen bleaching is realized.

CONCLUSIONS

1. Unbleached Kraft Pulp of Bamboo & Mixed Hard Wood blends of Kappa Number of 26 ± 3 can be bleached by 1st oxygen stage to reduce Kappa Number by 40 to 45% without adversely affecting pulp strength.
2. The oxygen bleached pulp when further bleached by C-E-H-H sequence yields pulp comparable to straight C-E-H-H bleached pulp with respect to strength and yield.
3. The chlorine demand to bleach oxygen bleached pulps by further C-E-H-H to around 80°GE brightness, is substantially lower with corresponding reduction in pollution load of COD, BOD, colour and dioxins as compared to straight C-E-H-H bleaching. This is a very favourable feature, because reduction of pollution load is bound to become an essential requirement of all the integrated pulp & paper mills in India. The reduction expected is 40 to 50% with respect to COD, BOD and dioxins and 60 to 70% with respect to colour.

ACKNOWLEDGEMENT

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REFERENCES

1. Singh, R.P., editor, The Bleaching of Pulp, Tappi Press, 1979.
2. Fossum, G., Paper Technology, March, 1992.
3. Paul Wei - Cheng Ku etal, T. J., Vol. 75 No. 10, October, 1992.
4. Samuelson, O., TAPPI International Pulp Bleaching Conf., 1991, Stockholm, Sweden.
5. Berry, H.K., International Paper Maker, February, 1994.