

Alkali/oxygen delignification and bleaching of soda bamboo pulp (Part-I)

DWIVEDI, R. P., BHARGAVA, G. G., KAUL, S. S. & SINGH, MAN MOHAN*

UMMARY

Bamboo Soda cooking experiments were performed with varying percentage of sodium hydroxide and the resulting pulp was refined in a Sprout Waldron Disc Refiner. Bamboo refined pulps of Kappa No. 45.4 and 71.3 were selected for C/E/H Sequence bleaching and O/C/E/H Sequence bleaching.

Bamboo refined pulp (Kappa No. 45.4) was delignified with alkali/oxygen with varying percentage of alkali at low consistency (7%). Kappa No. of the pulp decreased appreciably with increase in alkali percentage but pulp brightness did not improve appreciably. The pulp evaluation data shows that Tensile Index and Tear Index decreases with increase in alkali percentage in oxygen delignification whereas burst index showed reverse trend.

Alkali/oxygen delignified pulps were bleached under C/E/H sequence. The caustic extracted effluent has high BOD (72.5%) and COD (55.7%) reduction as compared to C/E/H sequence. The total chlorine consumption for 78-80% P. V. pulp brightness decreased with increase in alkali percentage in alkali/oxygen delignification stage.

Bamboo refined pulp (Kappa No. 45.4) was also bleached under C/E/H sequence. This pulp has high total chlorine consumption as compared to O/C/E/H sequence. Pulp shrinkage (%) and viscosity in O/C/E/H sequence bleached bamboo pulp > C/E/H bleached pulp and reverse trend was observed with copper no, P.C. No., decreased with increase in alkali (%) during oxygen delignification followed by C/E/H sequence, (O/C/E/H sequence). Tensile Index of O/C/E/H sequence bleached bamboo pulps > oxygen delignified pulp and C/E/H bleached pulp. Tear index of O/C/E/H sequence < oxygen delignified pulp. It was also observed that Tensile Index of alkali oxygen delignified pulp improved followed by C/E/H sequence bleaching.

Soda-Bamboo refined pulp with higher Kappa No. (71.5) also alkali/oxygen delignified. There was no significant improvement in pulp brightness. Alkali-oxygen delignified pulp after chlorination and alkali extraction gives effluent which has higher BOD and COD than the effluent of Bamboo soda pulp having Kappa No. 45.4. The total bleach chemical consumption under O/C/E/H sequence of higher Kappa No. pulp was higher than the pulp with Kappa number. The P. C. No., pulp shrinkage (%) & copper no. of higher kappa no. pulp was higher than lower Kappa no. pulp under O/C/E/H bleaching sequence.

Tensile Index of O/C/E/H bleached pulp (higher Kappa No. pulp) was higher than its Alkali oxygen delignified pulp but burst Index of higher Kappa no. pulp was lower than the low Kappa No. pulp bleached under O/C/E/H sequence.

Molecular oxygen is a unique oxidizing agent. In the normal form of oxygen the electronically stable form two of the electrons are unpaired. It has a strong tendency to react with organic substances and radical chain reactions are initiated. Several intermediate i.e. peroxides, organic radical and hydroxy radicals are formed. These intermediates are non-specific oxidative agents and in

pulp bleaching it is necessary to control their formation if severe degradation of the cellulose is to be avoided.

In the middle of 1950's the Soviet Researchers Nikitin and Akim et al^{2,3} commenced investi-

*Research & Development Division.
Orient Paper Mills, Amlai (M. P.) India.

gations into the possibilities of using molecular oxygen together with alkali for the bleaching and refining of dissolving pulps. Further development on the oxygen bleaching was started in France at the beginning of 1960's. The object was to improve the process in such a way that it would be applicable to the bleaching of paper pulps and the detrimental effect of oxygen-alkali treatment on the strength would be eliminated. Robert and associates^{4,5} worked on several inorganic chemicals for inhibiting the formation of several intermediate compounds i.e. peroxide, organic radicals and hydroxy radical which have higher degradation effect on cellulose. They observed that $MgCO_3$ was the best.

Other researchers^{6,7,8,9} also found that Magnesium salts addition as carbohydrate degradation inhibitors is necessary in maintaining the strength properties of oxygen pulp at acceptable levels, especially for unbleached grades. It was also pointed out by others^{10,11,12} that if $MgCO_3$ was mixed up with pulp prior to $NaOH$, the viscosity and strength properties were improved quite substantially.

Environmental considerations are having a substantial influence on the development of technology for existing plants and new installations in the pulp and paper industry. At the same time, raw material and processing cost are on the increase. These problems have promoted much interest in search for novel sulfur-free pulping process which could offer the desired higher pulp yields and qualities and which are less polluting than the conventional Kraft process¹³. Among the various approaches investigated during the past two decades, the two stage oxygen pulping system seems to offer the most promising alternative to the existing kraft process in terms of yield and pulp qualities^{14,15}. Most of the recent work^{6,8,16-23} consists of soda cook to high yield followed by defibrization prior to oxygen delignification in one or several stages. Preliminary work on oxygen bleaching has been carried out at Forest Research Institute on soda pulps from *Eucalyptus Hybrid*²⁴ and Kinetics of oxygen-alkali delignification of high yield pulps²⁵. In the present study the effect of oxygen bleaching on high Kappa no. soda cook and low kappa no. soda cook has been carried out and compared with conventional bleaching sequence.

EXPERIMENTAL :

Caustic cooking of Bamboo chips ($-22+10$ mm size) was carried out using 15.0%, 16.0%, 17.0%, 19.0% and 21.0% alkali and bath ratio 1:4. Cooking conditions and results are recorded in

Table-1. The resulting pulps were passed through sprout waldran disc refiner at a clearance of 254 microns using refiner plate D2A-501. The refined pulps were analysed for Kappa number and yield (%).

Bamboo pulp of cook no. 5 (Table-1, Kappa No. 45.4) was bleached with oxygen at 7% consistency, using 2%, 3%, 4% and 5% alkali respectively $MgCO_3$ (0.5%) was added as inhibitor to check degradation of cellulose. Oxygen was injected at 120°C (9.0 Kg/cm² pressure) for 90 mts. through a non-return valve connected with the side flange of the digester. Shrinkage of pulp (%), Kappa No. and brightness of the pulps are given in Table-2. These oxygen pulps (Expts. No. 2-5) were beaten at 25, 35, 45 and 55°SR freeness in a laboratory valley beater. Standard sheets were made as per Tappi standards. Physical strength properties of oxygen bleached pulps are represented in figures 10-12.

Oxygen delignified pulps of (expts. No. 2-5) were further bleached under C/E/H sequence. The alkali stage effluents were analysed for BOD5 and COD. The bleached pulps were analysed for copper no. viscosity, P.C. no. and brightness. Bleaching conditions and results are recorded in Table-3.

Unbleached bamboo pulp (Cook no. 5) was also bleached under C/E/H sequence for comparison with O/C/E/H sequence bleached pulps. Bleached bamboo pulps were also beaten in laboratory valley beater at 25, 35, 45 and 55°SR freeness. Physical strength properties of oxygen bleached pulps, O/C/E/H sequence bleached pulps and C/E/H sequence bleached pulp are represented in figures 13-15.

Bamboo pulp of expt. No. 2 having higher Kappa No. (Table-1, Kappa No. 71.5) was also bleached with oxygen (Oxygen pressure 9.0 Kg/cm²) using 7% alkali, pulp consistency (7%) and reaction temperature 120°C. Oxygen was injected for a period of 90 minutes. Magnesium carbonate (0.5%) was added to avoid pulp loss. Shrinkage of pulp (%), Kappa No. and brightness of the pulp are recorded in Table-4. Oxygen bleached pulp was further bleached under C/E/H sequence using 9% chlorine in the first stage and 4% hypochlorite in the third stage bleaching BOD, COD and pH of alkali extracted effluent was also analysed (Table-5). The number of double folds of alkali/oxygen delignified pulp, O/C/E/H bleached pulps of lower & higher Kappa No. are recorded in Table-6 along with double folds, of C/E/H bleached pulp of lower Kappa number. Bleached pulp

TABLE-1 CAUSTIC COOKING OF BAMBOO CHIPS

S No.	Particulars	Expt. No. 1 Bamboo (100%)	Expt No. 2 Bamboo (100%)	Expt. No. 3 Bamboo (100%)	Expt. No. 4 Bamboo (100%)	Expt. No. 5 Bamboo (100%)
1.	Weight of chips taken in kgm (O.D. basis)	2.5	2.5	2.5	2.5	2.5
2.	Caustic applied (%)	15.0	16.0	17	19	21
3.	Bath ratio	1:4.0	1:4.0	1:4.0	1:4.0	1:4.0
4.	Cooking cycle					
i)	Upto 135°C (mts)	60	60	60	60	60
ii)	At 135°C (mts)	60	60	30	30	30
iii)	From 135-165°C (mts)	60	60	60	60	60
iv)	At 162°C (mts)	90	90	120	120	120
v)	Total cooking time (mts)	270	270	270	270	270
5.	Yield (%)**	55.92	55.44	52.21	48.88	47.78
6.	Kappa No.	76.20	71.5	62.1	58.4	45.4
7.	Black liquor characteristics.					
i)	°TW at 60°C	9.0	10.5	12.5	13.5	16.5
ii)	R.A.A. as Na ₂ O(g/L)	10.5	11.0	12.52	15.5	17.05
iii)	Inorganic (%)	25.55	26.08	25.65	27.73	28.73
iv)	Organic (%)	74.45	73.92	74.35	72.27	71.17
v)	Total solid (%)	13.28	13.51	15.79	20.78	21.37

** Bamboo pulp from cook No. 1 to 5 were passed through sprout waldron disc refiner at clearance of 254 microns.

TABLE-2 OXYGEN BLEACHING OF CAUSTIC COOKED PULP
(KAPPA No. 45.4) — (TABLE 1 Expt. 5)

S. No.	Particulars	Expt. No. 2	Expt. No. 3	Expt. No. 4	Expt. No. 5
1.	Pulp taken in gms (O.D. basis)	800.0	800.0	800.0	800.0
2.	Consistency of pulp (%)	7.0	7.0	7.0	7.0
3.	Caustic applied (%)	2.0	3.0	4.0	5.0
4.	Magnesium carbonate added (%)	0.5	0.5	0.5	0.5
5.	Oxygen injected at 120°C (kg/cm ²)	9.0	9.0	9.0	9.0
6.	Oxygen passed (mts)	90	90	90	90
7.	Kappa no. of pulp	28.3	26.3	23.6	20.1
8.	Brightness of pulp (%) P.V.	25.0	26.0	28.5	29.5
9.	R.A.A. (g/L)	1.50	1.55	2.32	3.5
10.	Shrinkage of pulp (%)	1.05	1.53	2.75	3.87

TABLE—3. BLEACHING OF BAMBOO OXYGEN PULP UNDER C/E/H SEQUENCE

S.No.	Particulars	Bamboo Pulp (under Table 1 Expt. 5)	Oxygen treated Bamboo Pulp			
		Expt. No. 1	Expt. 2	Expt. 3	Expt. 4	Expt. 5
1. Chlorination Stage						
i)	Chlorine added % (on O D. pulp)	9.0	6.5	6.0	5.5	4.5
ii)	Chlorine consumed (%)	9.0	6.24	5.21	4.89	4.17
iii)	End pH	1.8	2.0	2.0	2.0	1.8
2. Alkali-Extraction Stage						
i)	Alkali-added (%)	2.5	2.5	2.5	2.5	2.5
ii)	BOD ₅ (mg/L)	440	260	220	160	120
iii)	COD (mg/L)	1900	1416	1058	940	841
iv)	End pH	10.8	10.5	11.2	11.3	11.6
3. Hypochlorite Stage						
i)	Hypochlorite added (%) as available chlorine	6.5	4.0	3.0	3.0	2.5
ii)	Hypochlorite consumed (%)	6.00	2.43	2.41	2.08	1.35
iii)	Pulp brightness (%) P.V.	77.0	78.0	77.5	80.0	77.0
iv)	End pH	7.7	7.9	7.7	7.8	7.6
v)	Pulp loss (%)	11.25	10.5	10.1	9.5	9.05
vi)	P.C. Na.	8.29	5.47	3.58	1.87	1.56
vii)	Viscosity of pulp (0.5% cps)					
	CED	5.63	6.53	6.91	6.35	7.29
viii)	Copper No.	1.720	1.336	1.272	1.372	1.245
4. Final Results						
i)	Total chlorine added (%)	15.50	10.50	9.00	8.50	7.00
ii)	Total chlorine consumed (%)	15.00	8.67	9.63	6.97	5.52
iii)	Total pulp shrinkage %)					
	oxygen + CEH sequence	11.25	11.55	11.63	12.25	12.92

Constant conditions :

Bleaching stage	C	E	H
Consistency of pulp (%)	3	5	5
Time (mts)	60	60	120
Temperature °C	27±1	50±1	40±1

Table—4. OXYGEN BLEACHING OF BAMBOO PULP OF HIGH KAPPA NO. (KAPPA No. 71.5)

S No.	Particulars	Bamboo pulp cook No. 2
1.	Pulp taken in gms	1000.0
2.	Consistency of Pulp (%)	7.0
3.	Magnesium carbonate added (%)	0.5
4.	Alkali added (%)	7.0
5.	Oxygen injected at 120°C (Oxygen Pressure 9Kg/cm ²)	9.0
6.	Oxygen injected (mts)	90
7.	Brightness of pulp (%) PV	25.0
8.	Initial pulp brightness (%)	23.0
9.	R.A.A. of wash liquor (g/L)	3.1
10.	Shrinkage of pulp	4.35
11.	Kappa No.	37.82

TABLE—5 BLEACHING OF BAMBOO OXY-GEN PULP (KAPPA No 37.82) UNDER C/E/H SEQUENCE

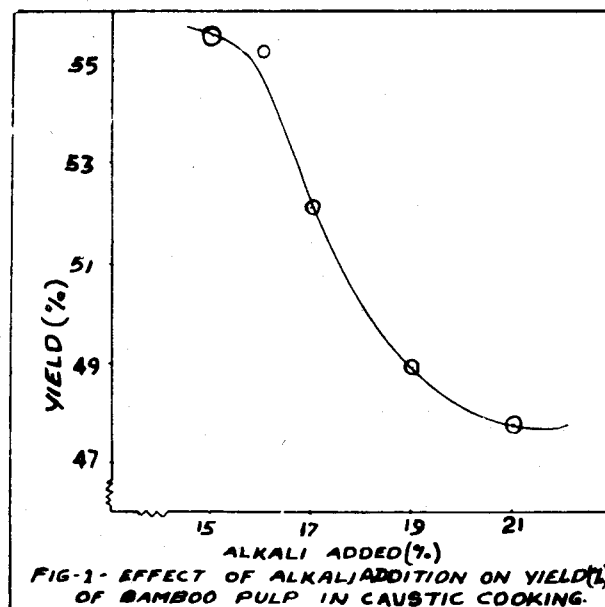
Sl. No.	Particulars	Cook No. 2
1.	Chlorination Stage	
i)	Chlorine applied (%)	9.0
ii)	Chlorine consumed (%)	8.83
iii)	End pH	1.8
2.	Alkali Extraction Stage	
i)	Alkali added (%)	2.5
ii)	BOD 5 (mg/L)	280
iii)	COD (mg/L)	1428
iv)	End pH	10.4
3.	Hypochlorite Stage	
i)	Hypochlorite added (%)	4.0
ii)	Hypochlorite consumed (%)	2.93
iii)	Pulp brightness (%) P.V.	76.0
iv)	End pH	8.3
v)	Pulp loss (%)	10.3
vi)	P.C. No.	3.86
vii)	Viscosity of pulp (0.5% CED) cps	6.26
viii)	Copper No.	1.245
4.	Final results	
i)	Total chlorine (%) added	13.0
ii)	Total chlorine consumed (%)	11.76
iii)	Total pulp loss (%) oxygen + C/E/H stage	14.38

was analysed for copper number, viscosity, P.C. No. and brightness. Oxygen bleached pulp and O/C/E/H bleached pulps were evaluated for physical strength properties. Physical strength properties of oxygen pulp and O/C/E/H pulps are represented in figs. 16-18.

DISCUSSIONS :

Soda cooking experiments of bamboo chips with varying percentage of alkali were carried out and the effect of alkali addition on pulp yield is depicted in fig. 1. It varied from 56% to 47% with alkali ranging from 15 to 21% as NaOH. The effect of alkali addition on Kappa No. of pulp (Fig. 2) show that Kappa no. decreases with increase in alkali percentage. Black liquor analysis of these cooking experiments. (TABLE-1) reveals that °TW, R.A.A. & total solids increased as expected with increase of cooking chemical.

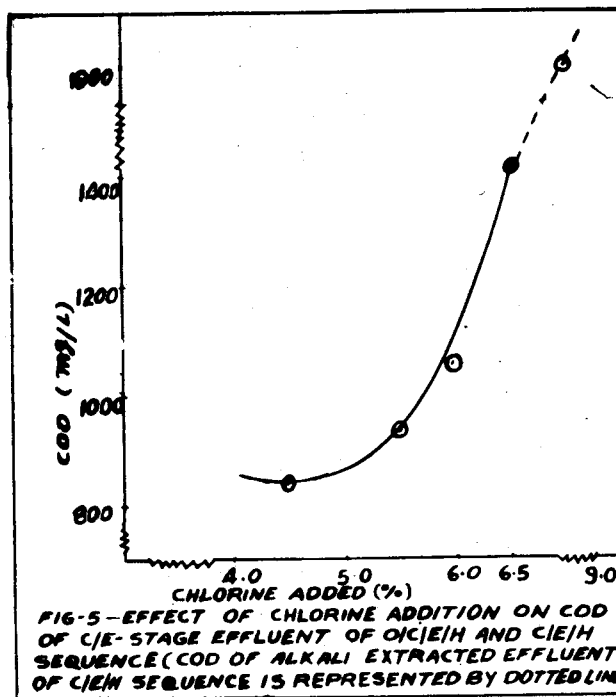
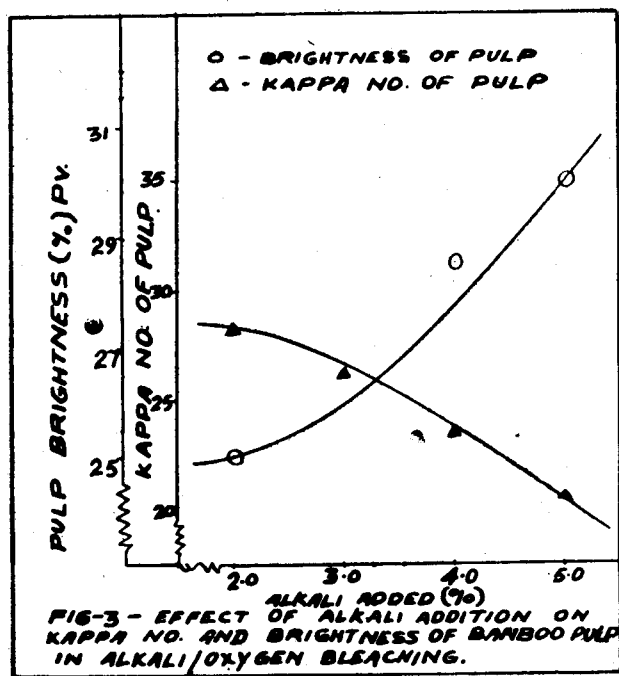
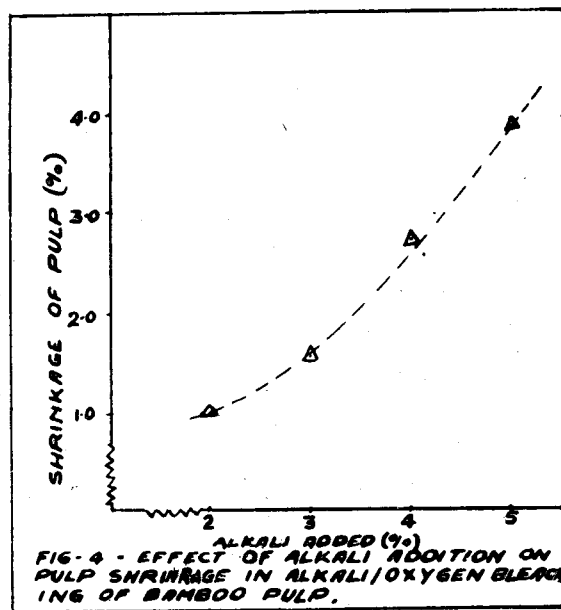
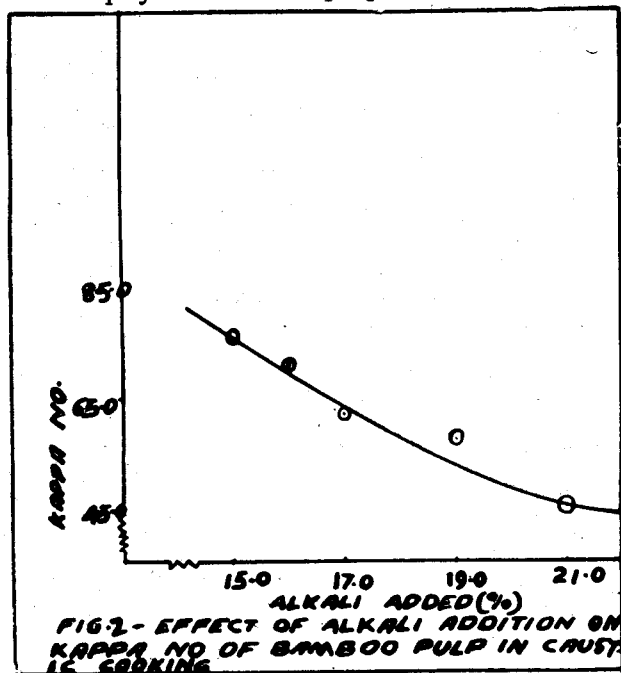
Two competing reactions delignification and carbohydrate degradation occur simultaneously during oxygen bleaching²⁶. Degradation of wood polysaccharide occurs due to oxidative hydrolysis which depends on both temperature and alkali concentration²⁷⁻²⁸. Bamboo refined pulp (Kappa No. 45.4) was delignified with alkali/oxygen using 2.0%, 3.0%, 4.0% and 5.0% alkali to find out optimum alkali dose (Table-2). The effect of alkali addition in oxygen delignification on Kappa No. of pulp and brightness is shown in Fig. 3. Kappa No. of the pulp reduced sharply with 2% alkali and then steadily upto 5% alkali. The brightness



of the pulp improved moderately which is caused by delignification and not by lignin bleaching²⁹. The effect of alkali/oxygen delignification on pulp shrinkage (%) is represented in Fig. 4.

Alkali/oxygen delignified pulps were evaluated for physical strength properties. The effect of

beating these pulps at different freeness on tensile index depicted in Fig. 10, shows that tensile index decreased with increase in alkali percentage. Burst index of these pulps increased with increase in alkali percentage (Fig. 11). Tear index was much affected in alkali/oxygen delignification as depicted in Fig. 12. Lower tear index is being a property which is adversely affected by oxygen bleaching



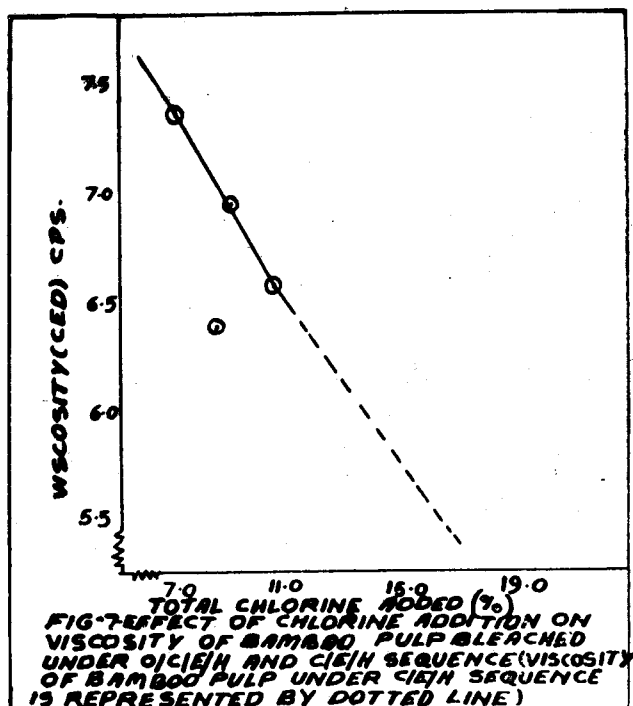
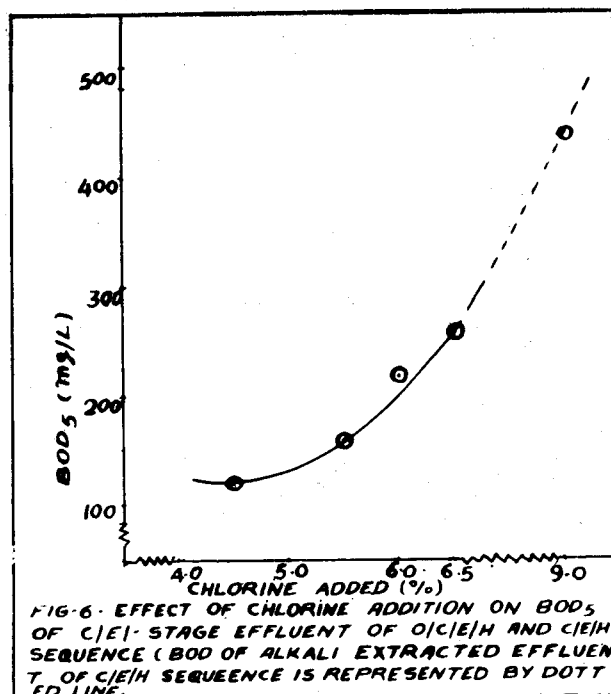
treatment³⁰. Double folds of alkali/oxygen delignified pulps increased with increase in alkali addition.

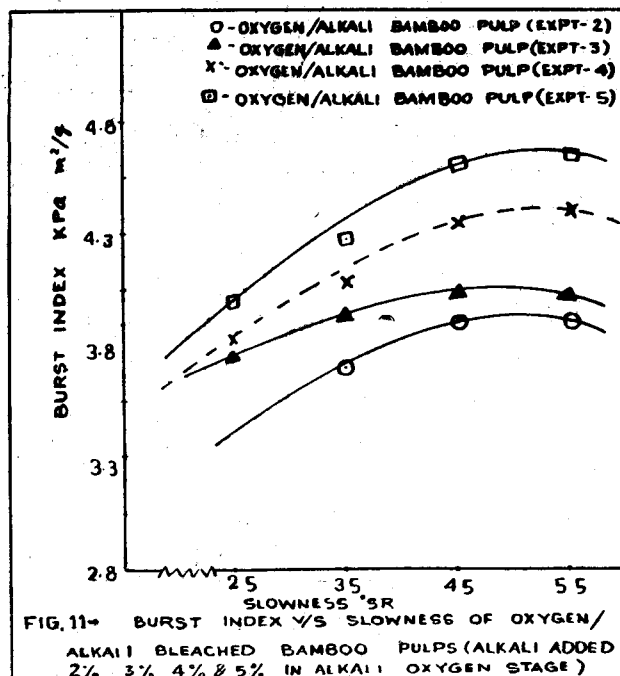
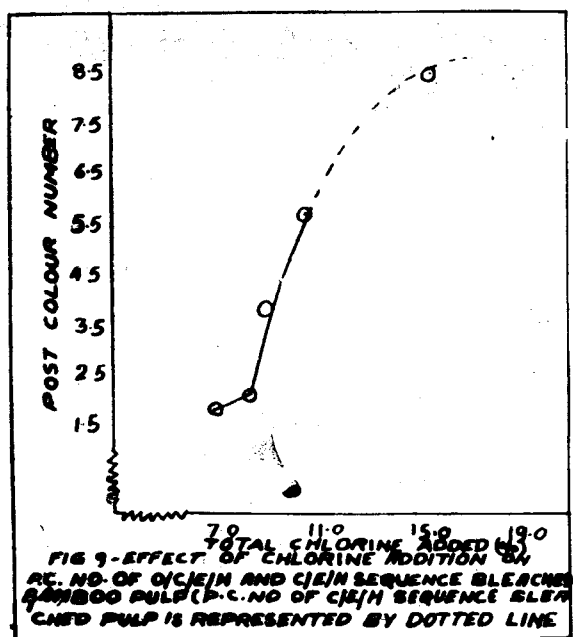
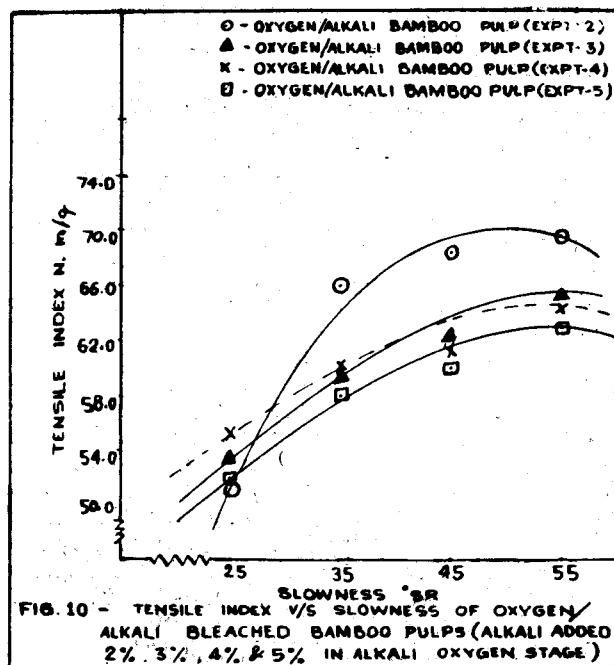
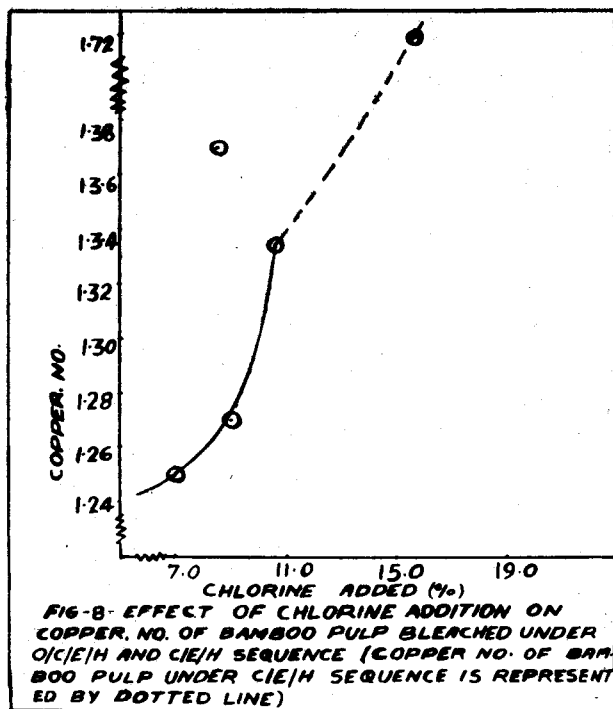
Oxygen stage bleaching is the only solution when the aim is for complete removal of colour, lowering of BOD and toxic elements in effluent from fully bleached pulps. Application of chlorine chemicals³¹ results in higher brightness pulps. Therefore alkali/oxygen delignified pulps were bleached with different chlorine and hypochlorite dosages in First and Third stage respectively. After alkali extraction the caustic extracted effluents of these pulps were analysed for BOD 5 and COD as per standard methods³². The effect of chlorine addition on COD and BOD 5 of caustic extracted effluent is represented in Fig. 5 & 6 respectively. Blank experiment for bleaching the soda bamboo pulp under C/E/H sequence was also carried out. COD and BOD 5 of caustic extracted effluent of blank experiment are depicted by dotted lines in fig. 5 & 6 respectively. COD reduction in O/C/E/H sequence (Expt. No. 2-5) was 25.5%, 44.3%, 50.5%, and 55.7% respectively, whereas BOD 5 reduction was 31.9%, 50.0%, 63.6% and 72.7% respectively as compared to C/E/H sequence. The total chlorine consumption in Blank experiment under C/E/H sequence was higher as compared to O/C/E/H sequence bleached pulps (Table-3).

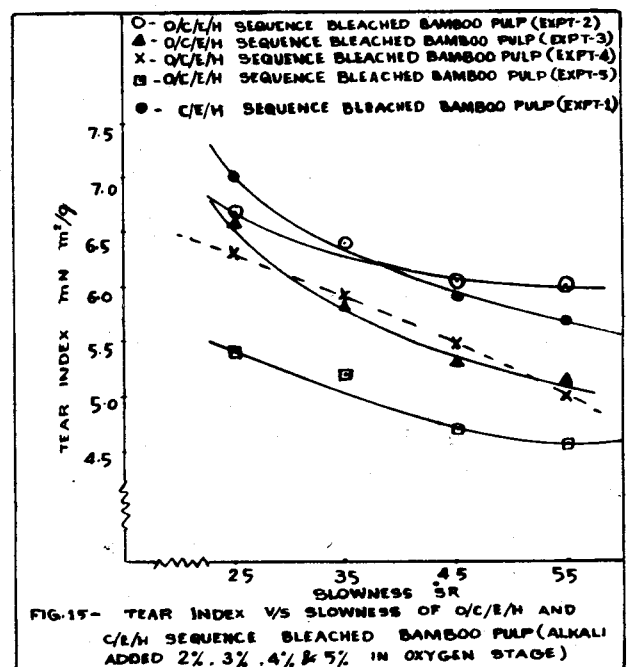
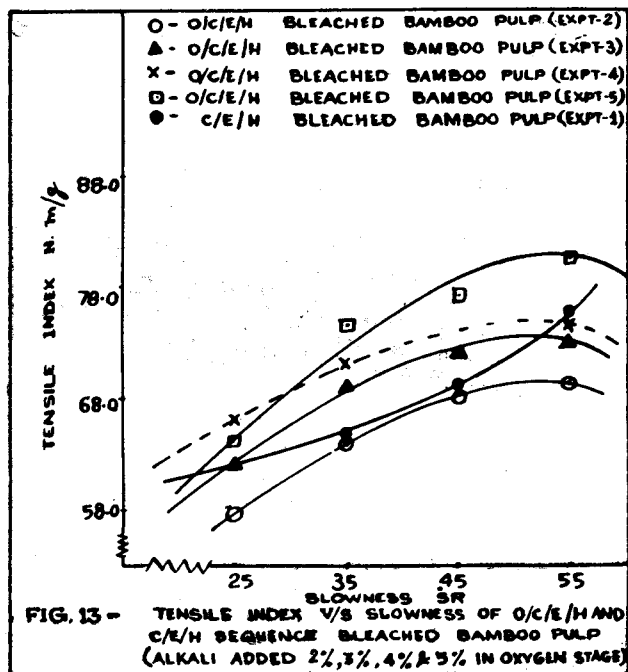
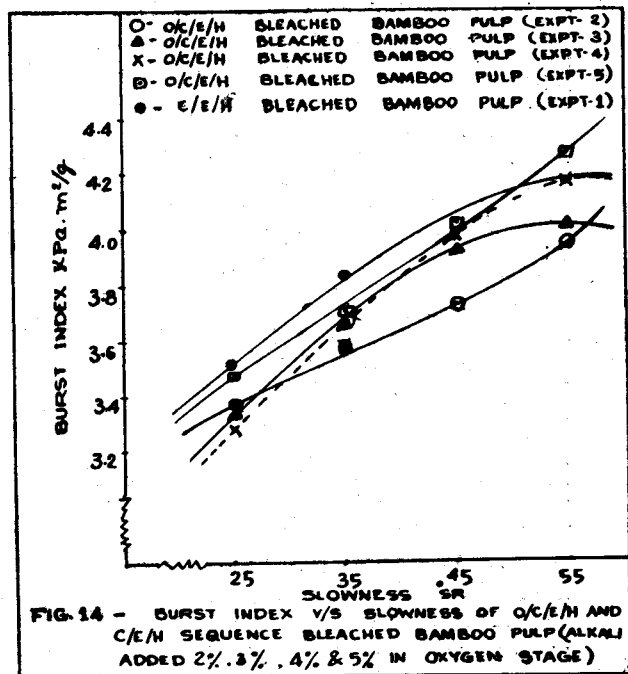
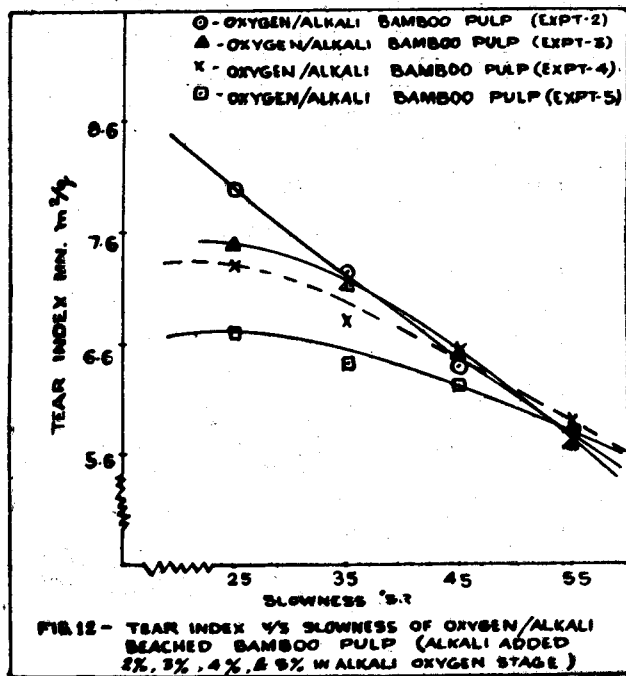
The effect of total chlorine addition on viscosity & copper no. of O/C/E/H sequence bleached pulp projected in Fig. 7 & 8 (Dotted lines of these figures indicated viscosity & copper no. of C/E/H sequence bleached pulp) show that viscosity of O/C/E/H pulps was higher than C/E/H pulp and reverse trend was observed with copper no. & P.C. No. Oxygen bleached pulps have better brightness stability than conventional bleached pulp³³. The total pulp shrinkage in O/C/E/H sequence was higher than C/E/H sequence.

This shown that the pulp degrade to a lesser degree when oxygen stage of bleaching is applied.

The effect of C/E/H and O/C/E/H sequence bleached pulps at different freeness against tensile index depicted in Fig. 13 shows that tensile index of O/C/E/H sequence bleached pulps increased with decrease in total chlorine consumption. Tensile index of O/C/E/H bleached pulps was higher than oxygen delignified pulps. Effect of beating of O/C/E/H bleached pulps on burst index at different freeness represented in Fig. 14 shows that burst index increased with decrease in total chlorine consumption. Beating of O/C/E/H and C/E/H sequence bleached pulps at different freeness







against tear index as shown in Fig. 15 indicates that tear index of O/C/E/H bleached pulps is lower than C/E/H and alkali/oxygen delignified pulps.

Soda-Bamboo pulp having higher Kappa No. 71.5 was also delignified with Alkali/oxygen which reduced Kappa No. 37.8 and pulp shrinkage was 4.35%. Results & conditions are recorded in Table-4. This pulp was bleached under C/E/H sequence. The alkali extracted effluent has high BOD₅ and COD (Table-5) as compared to lower Kappa No. bleached pulps effluent under same bleaching sequence. The total chlorine consumption and shrinkage (%) for higher Kappa no. bleached pulp under O/C/E/H sequence was higher than lower Kappa no. pulp under same bleaching sequence. The bleaching conditions and results for higher Kappa no. pulp under O/C/E/H sequence are recorded in Table-5.

The effect of beating alkali/oxygen delignified pulp and O/C/E/H sequence bleached pulp of higher Kappa no. at different freeness against Tensile index projected in Fig. 16 shows that O/C/E/H bleached pulp has tensile index > alkali oxygen delignified pulp < C/E/H and O/C/E/H bleached pulp of lower Kappa No. The effect of beating of Alkali/oxygen delignified and O/C/E/H pulp on burst index depicted in figure 17 indicates that burst index of higher Kappa No. oxygen delignified pulp was nearly equal to oxygen deli-

gnified and C/E/H bleached pulp of lower Kappa No. whereas it was > O/C/E/H bleached pulp of lower Kappa no. Tear index of alkali/oxygen delignified pulp of higher Kappa no. beaten at different freeness and represented in Fig. 18 shows that this pulp has tear index alkali/oxygen deligni-

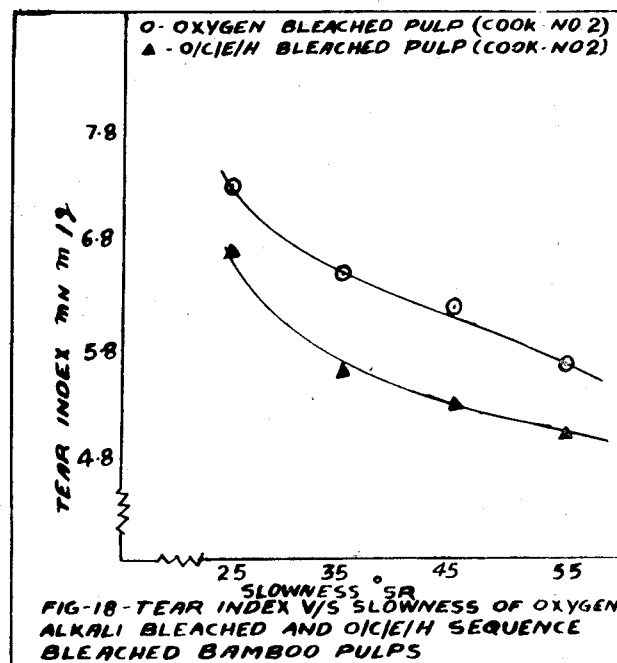
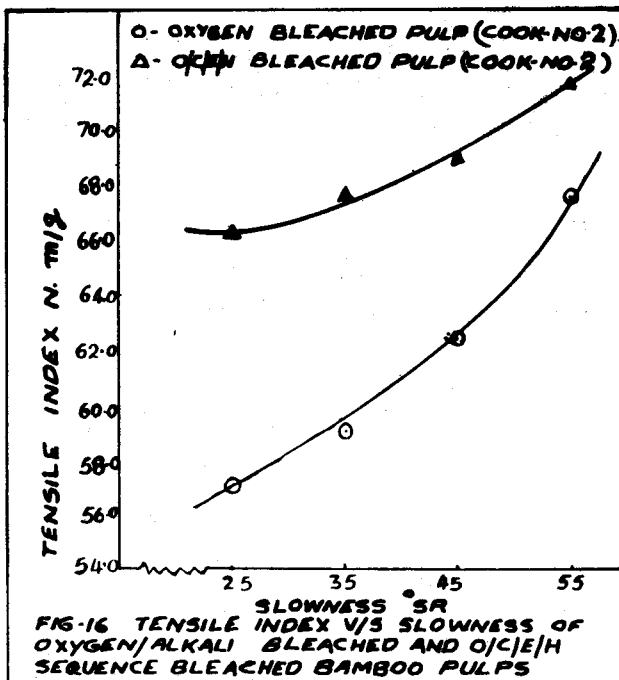
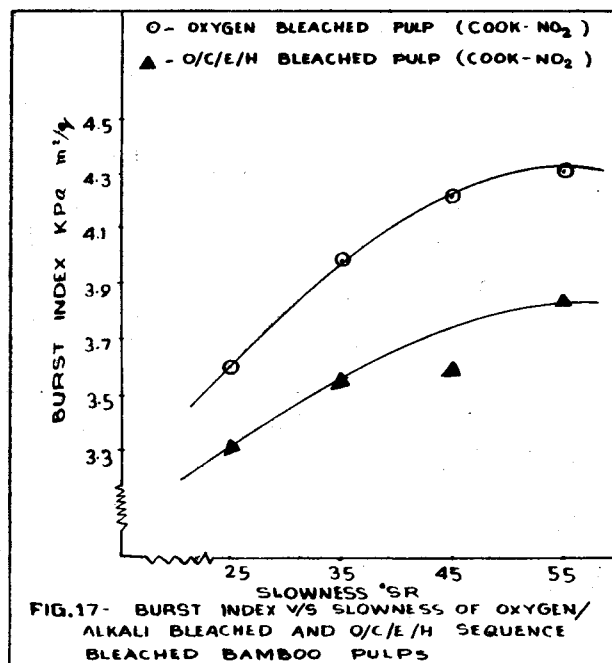


TABLE-6 NUMBER OF DOUBLE FOLDS OF ALKALI/OXYGEN, C/E/H AND O/C/E/H SEQUENCE BLEACHED PULPS BEATEN AT DIFFERENT FREENESS °SR.

S. No	Bleaching Expt. & Sequence followed	Double fold of Pulps beaten at freeness °SR			
		25	35	45	55
1.	Alkali/Oxygen Bamboo Pulps (Cook No. 5, Table-2)				
	i) Experiment No. 2 (2% alkali used)	90	145	150	175
	ii) Experiment No. 3 (3% alkali used)	250	270	300	320
	iii) Experiment No. 4 (4% alkali used)	325	390	450	485
	iv) Experiment No. 5 (5% alkali used)	280	330	340	360
2.	Alkali/Oxygen Bamboo Pulp (Cook No. 2, Table-4)				
	i) Experiment No. 1 (7% alkali used)	185	240	250	295
3.	C/E/H Sequence Bleached Pulp (Cook No. 5, Table-2)				
	i) Experiment No. 1	140	160	175	225
4.	O C E/H Sequence Bleached Pulp (Cook No. 5 Table-3)				
	i) Experiment No. 2	105	135	140	145
	ii) Experiment No. 3	110	155	160	165
	iii) Experiment No. 4	100	142	165	180
	iv) Experiment No. 5	55	85	90	105
5.	O/C/E/H Sequence Bleached Pulp (Cook No. 2, Table 5)				
	i) Experiment No. 1	100	135	165	170

gnified pulp of lower Kappa and > C/E/H bleached pulp of lower Kappa No. The O/C/E/H bleached pulp of higher Kappa no. has number of double folds nearly equal to O/C/E/H bleached pulps and < C/E/H bleached pulp of lower Kappa No. (Table-6). Beating time of alkali/oxygen delignified pulp of higher Kappa no. alkali oxygen delignified pulps and C/E/H bleached pulp of lower Kappa No. The O/C/E/H bleached pulp of higher Kappa No. takes lesser time in beating than C/E/H and alkali/oxygen delignified pulps of lower Kappa No.

CONCLUSION :

The lower Kappa No. Bamboo refined pulp bleached under O/C/E/H sequence give pulp of high brightness, lower P. C. No. and good physical strength properties. The BOD₅ and COD of the alkali extracted effluent were reduced in with increase in alkali addition (%) in alkali/oxygen

stage followed by C_iE/H sequence. The O/C/E/H bleached pulps takes lesser time in beating than C/E/H bleached pulp. The higher Kappa No. Bamboo refined pulp bleached under O/C/E/H sequence give pulp of high pulp brightness and satisfactory physical strength properties but the BOD, COD of alkali extracted effluent were higher as compared to lower Kappa No. bleached pulp effluent of O/C/E/H sequence. The physical strength properties of the bleached pulp under O/C/E/H sequence were inferior to lower Kappa No. bleached pulp. Pulp shrinkage in higher Kappa no. bleaching under O/C/E/H sequence was also high.

ACKNOWLEDGEMENT

The authors wish to express their gratitude to Shri I. M. Bhandari, Executive Vice-President, Orient Paper Mills' Amlai for his kind permission to publish these findings.

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