Research and Experience on the Bleaching of Bamboo Kraft Pulps

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The paper gives a detailed account of successful laboratory research and mill trials on the bleaching of bamboo kraft pulps at Central Pulp Mills. The attempts by the mills to continually upgrade their pulp quality, i.e. to produce pulps of good strength and brightness stability are described at length.

Todate, Cental Pulp Mills, popularly known as Cenpulp, are the only organisation in the world manufacturing and offering flash-dried paper grade bamboo kraft pulps–unbleached, semi-bleached and bleached to both the domestic and international markets. This being the case, a lot of laboratory research had to be undertaken to determine the optimum cooking and bleaching conditions to produce pulps of good strength and brightness stability. The laboratory results were subsequently confirmed in mill trials. The present paper gives a brief account of the findings, with particular emphasis on brightness stability.

Effect of Permanganate Number on Pulp Bleachability and Brightness Stability

Most Indian paper mills cook bamboo to a K. No. of 20–24; there are some mills, however, cooking to a K. No. of 14–18, especially for bleachable grades.

Table 1 lists the cooking conditions, physical and chemical characteristics of unbleached and bleached bamboo kraft pulps at two levels of permanganate numbers, viz. K. Nos 13.5 and 22.0. The former is laboratory cooked pulp and the latter is mill cooked pulp. TAA requirement for the lower K. No. pulp is 25% more; the unbleached pulp yield is 44.5%, compared to 48.8% for the high K No. pulp. Fiber classification (Clark) shows significant differences in the characteristics of the low and high K No. pulps. The —125 fraction is about 8% higher in the high K. No. pulp. The organics in the black liquor of the low K. No. pulp are about 5% higher than in the case of the

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TABLE 1 : Cooking Conditions, Chemical and Physical Properties of Unbleached Bamboo Kraft Pulps of Permanganate Numbers 13.5 and 22.0

Particulars			Permanganate No. 13.5 (LAB Cook)	Permanganate No. 22.0 (Mill Cook)
A.	**Cooking Conditions :**			
	Chemicals on OD Chips TAA (As Na_2O)	%	20.0	16.0
	Time to Max. temp.	Min.	150	150
	Time at Max. temp.	"	120	90
	Max Temp.	°C	165	160
	Bath ratio (Chips to liquor)		1:2.5	1:2.5
B.	**Unbleached Pulp Yield**	%	45.5	48.8
C.	**Chemical Properties :**			
	Ash	%	2.5	2.7
	1% NaOH solubility	%	6.1	9.0
	Lignin	%	3.9	6.1
	Pentosans	%	15.5	16.8
D.	**Fiber Classification (At Initial Freeness) (Clark)**			
	+ 20 mesh	%	51.5	38.5
	— 20+ 50 mesh	%	17.3	22.5
	— 50+ 65 mesh	%	7.4	7.5
	— 65+125 mesh	%	4.5	4.5
	—125 mesh	%	19.3	27.0
E.	**Black Liquor Analysis**			
	a) Organics/Inorganics (as such at 900°C)	%	60/40	54/46
	b) Calorific value	Btu/lb	6340	6090
	c) Free alkali as NaOH	gpl	9.6	6.0
	d) pH		12.2	11.4

high K.No. pulp. The bamboo (Dendrocalamus strictus) chips in the present study have 30% moisture. Chips classification yields 95% acceptable chips (–28 mm to + 4 mm).

Table 2 gives the bleaching conditions as well as the bleached pulp characteristics of the low K. No. pulp (K. No. 13.5). The pulp was bleached in CEHH, CHEH, CEHP and CEHD sequences. Lowest Pc number as well as highest pulp strength were achieved in CEHD sequence, followed by CEHP, CHEH and CEHH sequences.

The bleaching conditions and the bleached pulp strengths for high K. No. pulp (K. No. 22.0) are given in Table 3.

As noted in Table 2, CEHD pulp had the lowest Pc value and the highest over-all strength. However, at the same brightness level, Pc number is higher for the high K. No. pulp in each bleaching sequence. For instance, in CEHH sequence, 22 K. No. pulp had a Pc number of 8.7 as against a Pc number of 5.9 for 13.5 K. No. pulp.

It can be also seen from the results of Tables 2 and 3 that pulping to a low K. No. results in an effluent of lesser colour, TSS, BOD and COD. For example, in CEHH sequence, BOD_5 values in chlorination, extraction, hypo I and hypo II stages were 37 PPM, 80 PPM, 37 PPM and 10 PPM respectively for the low K. No. pulp, compared to the corresponding figures of 82.5 PPM, 120 PPM, 58 PPM and 35 PPM respectively for the high K. No. pulp. This means a better effluent quality and lower pollution load to the sewer in low K. No. pulps. It is worth mentioning here that CHEH sequence gave an effluent of the lowest colour.

Effect of Different Chemicals on Pulp Brightness and Colour Reversion

The effect of H_2O_2, $NaHSO_3$, HCl, H_2SO_4 and $NaBH_4$ on bleached pulp brightness and reversion is shown in Table 4. Pulps of 76–80 PV (CEHH) brightness were taken in this study. As could be expected, application of H_2O_2, $NaHSO_3$ and $NaBH_4$, although expensive, increased pulp brightness and reduced Pc number. It is interesting to note that acidification of the final bleached pulp (CEHH) with HCl or H_2SO_4 0.10-0.50% on pulp) increased pulp brightness by over 2 points and reduced post colour number by (about 30%.

Effect of Sulfamic Acid in Hypochlorite Bleaching

The beneficial effect of sulfamic acid in hypo bleaching is outlined in Table 5. Bleached pulps produced under the following conditions were compared : 1) No caustic or no sulfamic acid as buffer, (pH not controlled during bleaching) 2) caustic alone used as buffer and 3) sulfamic acid used in place of caustic. Sulfamic acid treated pulp had the highest viscosity. The Pc number of the SA treated pulp is about same as caustic buffered pulp but around 2.0 points lower than that of the unbuffered pulp. The over-all pulp strengths of the sulfamic acid treated and caustic buffered pulps are about the same, both being higher than those of the unbuffered pulp.

A Brief Summary of Miscellaneous Work Done at Cenpulp Research Laboratory on pulp Bleaching.

1. **Chlorination Time**
   For pulps of around 20 K. No., 95% of chlorine added was consumed in 30 min.
2. **Effect of % NaOH in Extraction**
   Increased caustic (in the range of 1 to 4% on pulp) decreases reversion. Around 2.5 % NaOH appears to be the economic optimum.
3. **Effect of Extraction Temperature**
   Extraction temperatures in the range of 40 to 70°C were studied. 60°C was found to be the optimum.
4. **Effect of Hypo Addition in Extraction**
   0.5% and 1.0% hypo as available chlorine were added in the extraction stage. Nothing conclusive resulted in respect to pulp brightness, reversion or strength.
5. **Effect of Hydrogen Peroxide in Extraction**
   The effect of using H_2O_2 in extraction stage in the range of 0.25—1.0% on pulp was

TABLE 2

Bleaching Conditions and Results for Various Sequences (K. No. 13.5) LAB Cook

Bleaching Conditions :

Bleaching sequence		C	E	H	H	C	H	E	H	C	E	H	P	C	E	H	D
Chemicals on OD Pulp	%	4.0	1.75	2.0	0.25	4.0	1.5	1.5	1.5	4.0	1.75	2.0	0.3	4.0	1.75	1.5	1.0
Consistency		2	10	10	10	2	10	10	10	2	0	10	10	2	10	10	10
Temperature	°C	30	60	45	45	29	45	60	45	30	60	45	70	30	60	45	70
Retention time	Min.	30	90	150	180	30	150	90	180	30	90	150	120	30	90	150	60
pH		1.7	10.5	8.0	8.0	1.8	8.5	11.0	8.5	1.7	10.5	8.0	8.0	1.7	10.5	8.0	4.5
Bleaching losses on OD Pulp					10.2				10.0				9.8				9.6
Brightness	PV			76	80		56		80			73	80			73	82
Post colour Number					5.9				4.5				2.5				2.0
Viscosity (0.5% CED)	CPS				10.2				11.4				12.4				13.2
Copper number					1.60				1.55				1.50				1.45
Carbonyl	me/100g				15.8								13.2				12.7
Carboxyl	"				6.2								6.8				7.3

Effluent Characteristics :

Colour (Pt-Co units)	70	1400	60	10	75	500	350	30	80	1400	60	11	70	1400	45	12
pH	2.8	10.5	8.3	8.5	2.0	9.0	11.4	8.4	2.8	10.4	8	10	2.8	10.5	8.3	4.5
Total suspended solids PPM	120	180	104	160	136	152	232	130	124	288	132	200	120	180	104	110
BOD 5 days at 20°C PPM	37	80	37	15	38	115	79	8	30	85	30	12	37	80	37	8

Bleached Pulp Strength Evaluation At 250 ml CSF

Initial freeness	ml CS	680	720	680	690
Final freeness	ml CS	250	250	250	250
Breaking length	M	5335	5975	6750	7180
Burst factor	Mullen	47.1	49.5	52.4	53.1
Tear factor	Elm.	112.7	124.5	146.3	161.0
Double folds	MIT	169	190	244	347

Table 3 : Bleaching Conditions And Results For Various Sequences (K. No. 22.0) Mill Cook

Bleaching Conditions :																
Bleaching Sequence	C	E	H	H	C	H	F	H	C	E	H	P	C	E	H	D
Chemicals on OD Pulp %	8.0	2.5	3.0	0.5	8.0	2.0	2.5	2.5	8.0	2.5	3.0	1.0	8.0	2.5	2.7	1.0
Temperature °C	27	60	45	45	27	45	60	45	27	60	45	45	26	60	45	45
Retention time Min.	30	90	150	180	30	150	90	180	30	90	150	120	30	90	150	120
pH	1.7	11.0	8.0	8.0	1.7	8.0	10.0	8.0	1.7	11.0	8.0	11.0	1.7	11.0	8.0	5.0
Bleaching losses on OD pulp				15.6				14.9				14.7				14.4
Brightness PV			76	80.5		41	42.5	80.5			76	81.0			75	80.0
Post colour number				8.7				7.4				3.9				3.5
Viscosity (0.5% CED) CPS				8.5				9.3				9.5				9.8
Copper number				1.65				1.67				1.63				1.64
Carbonyl me/100g				21.0								17.1				15.0
Carboxyl				6.8								6.9				7.0
Effluent Characteristics :																
Colour (Pt–Co units)	250	4250	45	15	250	900	1900	25	250	4250	40	25	250	4250	45	30
pH	1.8	9.6	8.0	8.3	1.8	11.2	8.0	8.5	1.8	9.2	8.4	10.5	1.8	9.6	8.0	4.6
Total suspended solids	310	504	576	684	85	425	405	565	452	632	660	480	316	504	576	125
BOD 5 days at 20°C PPM	82	120	58	35	86	110	43	12	85	130	58	26	82	120	58	30
Bleached Pulp Strength Propertise At 250 ml CSF																
Initial freeness ml CS				660				650				680				680
Final freeness				250				250				250				250
Breaking length M				5110				5855				6300				6410
Burst factor Mullen				42.3				44.2				43.9				44.0
Tear factor Elm.				87.1				92.7				87.1				106.2
Double folds MIT				83				97				106				117

Table 4

Effect of Different Reagents on Pulp Brightness And Colour

	Reversion Chemical % on OD pulp	Initial Brightness PV	Final Brightness PV	Post Colour Number
Permanganate No. 22.0	—	80	80	8.50
	0.1	80	81.5	5.30
H_2O_2	0.2	80	82.0	4.80
	0.5	80	83.0	4.30
	1.0	80	83.5	4.00
	—	79	79	8.10
$NaHSO_3$	0.1	79	81	5.26
	0.5	79	82	4.70
	1.0	79	82	3.94
	—	76	76	10.50
H_2SO_4	0.5	76	77.5	8.50
	1.0	76	78.5	7.50
HCl	—	78	78	14.19
	0.10	78	80	9.50
Sodium Borohydrate	—	76	76	6.60
Permanganate No. 13.5	0.1	76	78	2.30
	0.25	76	80	2.10
	—	77	77	8.60
Permanganate No. 22.0	0.1	77	78	4.43
	0.25	77	79	4.20

studied. In low K. No. pulps (less than 15.0), the use of H_2O_2 helped to reduce reversion to a higher extent than in high K. No. pulps. The higher the peroxide percent used, the lower the colour reversion.

6. **Effect of White Liquor in Extraction**

Plant white liquor (2% on pulp) compared favourably with NaOH (at the same level of application) regarding final pulp brightness and reversion. The extracted pulp should, however, be thoroughly washed to prevent carry over of too much sulphide, which could interfere with subsequent hypo bleaching.

7. **Effect of CHHEH Sequence**

This sequence gave a lower post colour numbor than CHEH sequence, but not that

Table 5

Effect of Sulfamic Acid in Hypochlorite Bleaching

Particulars		No NaOH No sulphamic acid.		NaOH as buffer. No sulphamic acid.		Sulphamic acid No NaOH	
		H_1	H_2	H_1	H_2	H_1	H_2
NaOH on OD Pulp	%	—	—	0.75	0.5	—	—
Sulphamic acid on hypo	%	—	—	—	—	4.0	4.0
Hypochlorite as available chlorine	%	2.5	1.0	2.5	1.0	2.5	1.0
Retention time	Min	120	150	120	150	120	150
Temperature	°C	45	45	45	45	45	45
Consistency	%	10.0	10.0	10.0	10.0	10.0	10.0
pH		6.4	6.2	8.2	8.0	6.3	6.0
Brightness	PV	72	80	71	79	73	80
Cost colour Number		15.0	10.0	13.5	8.2	12.9	8.1
Piscosity (0.5% CED) CPS			7.8	—	10.2	—	12.3
V% NaOH solubility	%		8.5		7.2		7.5
Copper Number			1.70		1.62		1.63
Strength Evaluation							
Initial freeness	ml CS	660			670		660
Final freeness	ml CS	250			250		250
Teating time	Min.	40			42		42
Breaking length	M.	5530			6270		6215
Burst factor	Mullen	52.8			55.2		54.3
Bear factor	Elm.	100.4			93.0		100.4
Double folds	MIT	635			810		740

Table 6

Physical And Chemical Properties of Different Pulp Grades Manufactured At Central Pulp Mills

Bleaching Conditions:

Bleaching sequence		C	E	H	H	C	E	H	H	C	E	H	H	C	E	H	H
Chemicals on OD Pulp	%	7.8	2.0	2.5	0.5	8	3.0	2.5	1.0	8	3.5	3.0	1.0	8	4.0	3.5	1.0
Temperature	°C	30	45	35	35	30	50	38	38	30	60	40	40	30	60	40	40
Retention time	Min.	20	120	120	150	20	120	120	150	20	120	120	150	20	120	120	150
Consistency	%	2	10	10	10	2	10	10	10	2	10	10	10	2	10	10	10
pH		1.8	8.9	6.5	7.5	1.8	10.0	7.5	7.5	1.8	11.2	7.5	7.5	1.8	11.2	7.4	7.5
Brightness	PV				55				65				72				80

Bleach Consumption (On OD unbleached pulp)

Chlorine consumption																	
1. In chlorination stage	%				7.7				7.9				7.9				7.9
2. In hypo Stage	%				2.8				3.3				3.7				4.2
Caustic	%				2.0				3.0				3.5				4.0
Sulfamic acid	kg/ton				—				0.7				0.8				1
Caustic as buffer	%				0.2				0.4				0.5				0.5
(When Sulfamic acid is not used)																	

Chemical Properties

Viscosity (0.5% CED)	CPS				16.0				14.6				13.0				12.0
Copper Number					1.57				1.60				1.63				1.65
Post colour number					20.4				14.6				10.9				8.5

Strength Properties (At 250 ml CSF)

Breaking length	M				6100				6500				5845				5780
Burst factor	Mullen				50.2				53.9				51.4				46.7
Tear factor	Elm.				152				146				136				120
Double folds	MIT				425				536				326				214

Note:—Cooking Conditions:

TAA 16% as Na_2O; Time to 105°C—60 min.; Time at 105°C—30 min.; Time from 105°C—160°C—90 min.; Time at 160°C—90 min.; Bath ratio (chips to liquor) 1:2.5 Unbleached pulp yield—48.8%. Permanganate number—22.0.

much lower to warrant an additional bleaching stage.

8. **Effect of Sulfamic Acid on Colour Reversion**

   Bleached pulps produced with caustic (as buffer) or sulfamic acid in hypo bleaching had almost identical post colour numbers.

9. **CEHDP Sequence**

   CEH pulp of 76 PV brightness and 11.4 Pc number was bleached with ClO_2 (1.0% on pulp). The resulting pulp had a brightness of 84 PV and Pc. number of 2.3. 1.5% H_2O_2 was then applied on this pulp at 70°C at 15% consistency for 150 min. to give a pulp of 87 PV brightness at a Pc number of 0.55. Following acidification with 1.0% H_2SO_4 on pulp, the pulp brightness was raised to 90 PV.

10. **CPHP Sequence**

    This sequence gave pulps of 80–82 PV brightness at a Pc number of 3.5, but H_2O_2 applied was rather high at 1.5% on pulp.

Mill Bleaching

Unbleached pulp (K. No. around 22) is bleached in CEHH sequence to different levels of pulp brightness. All the towers are of upflow type. Kamyr, Inc. are the suppliers of bleach plant.

The conditions of bleaching for pulps of 55 PV, 65PV, 72PV and 80PV brightness are given in Table 6. It has been repeatedly observed that over-all pulp strength is the highest for 65Pv brightness pulp in CEHH sequence.

The higher the pulp brightness, the lower the Pc number. For instance, the Post colour numbers of 55PV, 65PV, 72PV and 80PV brightness market pulps were 20.4, 14.6, 10.9 and 8.5 respectively.

Flash drying operation does not increase Pc number, as the pulp drying conditions and subsequent cooling before baling are so controlled to keep the reversion at a minimum. It is found that laboratory air dried and plant flash dried pulps of 80PV brightness have about the same Pc number.

Use of sulfamic acid in hypo-bleaching has helped to go in for higher temperatures in H_1 and H_2 stages without degrading the fiber, which means increased pulp production rates. Besides, an over-all savings of about Rs5/ ADT bleached pulp is obtained, when sulfamic acid is used in preference to caustic (as buffer) in hypochlorite bleaching.

That lower K. No. pulps give easier bleaching pulps of somewhat higher brightness stability was confirmed in mill experience. However, a production drop of about 20 percent was experienced when bleaching pulps of around 16 K. No., compared to pulps of around 22 K. No. The main difficulty was in handling higher black liquor solids in evaporators and in processing about 25 percent more TAA (white liquor) in the case of lower K. No. pulps.

Post colour number of pulp does not necessarily correlate with actual brightness drop in pulp storage. It has been repeatedly found that low Pc number pulps recorded a higher brightness drop during storage at higher relative humidity than did high Pc number pulps at lower relative humidity. Cenpulp experience has also shown that at the same brightness level for the same bleaching sequence, post colour number is about same in both pine and bamboo kraft pulps.

A Brief Description of Mill Trials on the Bleaching of Bamboo Kraft Pulps

1. **Mill Trial of CHEH Sequence**

   A bleached pulp of slightly better brightness stability and higher pulp strength and viscosity than in regular CEHH sequence was obtained. The effluent calour in CHEH is much lighter than in CEHH sequence. Laboratory research findings detailed in Tables 2 & 3 are essentially confirmed

2. **Mill Trial of CEHP Sequence**

   Application of H_2O_2 (1% on pulp) on the fourth stage increased the pulp brightness to 82PV, which on acidification with 0.5% H_2SO_4 (on pulp) gave a pulp of 84PV brightness at Pc No. of 3.0. The CEHH bamboo kraft pulp, for comparision, at 80PV brightness has a Pc No. of around 7.5. Using 1.0%

H_2O_2 on pulp, however, increases pulp cost by over Rs. 100/ton.

3. **Mill Trial Using H_2O_2 at the Screw Conveyer After Thune Press.**

   Bleached (CEHH) bamboo kraft pulp at 40% consistency was treated with 0.5% H_2O_2 on pulp. The brightness and Pc number of the untreated pulp were 80PV and 7.0 respectively. The brightness and Pc number of the H_2O_2 treated pulp were 81PV and 6.0 respectively.

   Actual brightness drops during storage for three months for the untreated and H_2O_2 treated pulps were 2.0PV and 1.5PV rerpectively. There was no real advantage on using H_2O_2 (0.5% on pulp) here.

Conclusions

1. The lower the K. No. of unbleached pulp, the lower the colour reversion of the bleached pulp. However, at lower K. No., pulp production rate drops in mill practice.
2. CHEH sequence is superior to CEHH sequence, as it yields a pulp of better brightness stability. The control of bleaching in just one H stage after extraction is, however, difficult.

   Also, CHEH sequence gives an effluent of lighter colour than in CHEH sequence.
3. Chlorine dioxide and Hydrogen peroxide can be advantagously employed to yield pulps of higher strength and better brightness stability. These chemicals are, however, very expensive.
4. Acid wash 0.1% to 0.5% HCl or H_2SO_4 on final bleached pulp) raises pulp brightness by about 2 points.
5. Sulfamic acid application results in a bleached pulp of good viscosity; also over-all savings in chemical cost in bleaching are about Rs.5/ADT of bleached pulp.
6. Under controlled bleaching conditions, the higher the pulp brightness the lower the post colour number.

   Post colour number is dependent on the relative humidity and temperature of the pulp storage atmosphere.

   A high post colour number at lower relative humidity often gives less brightness drop in a pulp than does a low Pc number at highter relative humidity.

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Acknowledgements

To Sarvashri S. J. Shah, K.H. Desai, A.R. Dharwadkar, D.G. Gandhi and K.H. Parekh for skilled experimental work.