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HYPOCHLORITE BLEACHING OF BAMBOO COLD SODA HIGH-YIELD PULP FOR NEWSPRINT FURNISH

Islam S., Bist V., Suresh Chand and Pant R.

Central Pulp and Paper Research Institute,
Dehradun 248 011.

Abstract

Cold soda bamboo high yield pulp has low initial brightness and high yellowness. Bleachability of this pulp with oxidative and reductive bleaching agents like calcium hypochlorite, hydrogen peroxide, dithionite and borohydride is poor due to presence of chromophoric groups namely carbonyl group. Calcium hypochlorite bleachability of this pulp is enhanced when the unbleached pulp is pre-treated with some chemicals. However, best result is obtained using sodium carbonate as "additive" during calcium hypochlorite bleaching. the enhanced bleachability is due to elimination of carbonyl groups following oxidation with "nascent" oxygen which is believed to be the active bleaching agent in sodium carbonate buffered calcium hypochlorite bleaching system. The probable reaction mechanism of carbonyl group oxidation is explained.

Introduction:

Bamboo and hardwoods are the two major fibrous raw materials used for the manufacture of various types of papers in India. In newsprint sector also, significant amount of bamboo is used and one newsprint mill is using 30-35% of bleached bamboo cold soda high-yield pulp in its composite fibre furnish[1]. Unbleached cold soda pulp of bamboo has brightness of 20 to 27% of ISO and yellowness of 51 to 63% depending upon age and storage life after felling. Strength properties of this pulp are quite satisfactory for newsprint but one inherent problem of this pulp is its poor bleachability and high yellowness. Even with 25% of calcium hypochlorite, brightness achieved under normal conditions is only 45% ISO[2]. Differences in bleaching response and yellowing of pulp are due to the chromophoric systems present in them. Such systems are either present in the raw material itself of are produced during pulping and bleaching. Virkola and Sihtola[3] have shown that carbonyl groups play a significant role in the yellowing of pulp. Giertz[4] has suggested that sum of the carbonyl and carboxyl contents of the pulp would determine its tendency to yellowing. Rapson and Hakim[5] have established that carbonyl groups contribute to a greater extent than carboxyl groups.

Infra-red spectra of thin sheets of bamboo cold soda pulp indicated[6] the presence of acetyl carboxylic structures,- unsaturated carbonyl, ring quinone and conjugated structures which are responsible for the poor bleachability and high yellowness of the pulp. Literature suggests that reductive bleaching agents like sodium borhydride and dithionite are effective in removing carbonyl groups are effective in removing carbonyl groups and improving bleachability of high-yield pulps. Studies carried out by T.K. Roy etal[6] showed that both borohydride and dithionite are ineffective in improving bleachability of cold soda bamboo pulp. It was observed that carbonyl was unaffected by dithionite and very high dosages of borohydride was required to effect attack on carbonyl structures. 6% Borohydride on pulp produced brightness gain of 7 units only. It was inferred by the investigators that the inability of dithonite and borohydride to reduce carbonyl structures to corresponding phenols was possibly due to the presence of substantial amount of condensed quinoid structures produced during alkaline pre-treatment followed by refining and also their specific hinderance due to neighbouring groups which make them resistent to attack. Hydrogen peroxide is also known to be capable of oxidising, Carbonyl group to carboxyl groups. Studies carried out by Mohan Rao etal[2] showed that bleaching response of cold soda bamboo pulp is very poor with hydrogen peroxide. Even with 5% H^2O^2 on pulp, brightness increase of only 5 units was achieved. The ineffectiveness of hydrogen peroxide can be attributed to the fact that though it oxidizes aldehydic carbonyl to carboxyls it brings about a simultaneous formation of new aldehydic and ketonic carbonyls[7]. Thus it is observed that conventional methods of bleaching lignin rich high-yield puls are ineffective in brightening bamboo cold soda pulp.

The present study investigates the possibilities of suitable "chemical pre-treatment" before bleaching or "additive" bleaching of bamboo cold soda pulp to improve its bleachability and reduce yellowness to be suitable for newsprint. The pulp brightness target set for the study is 55% ISO and calcium hypochlorite was chosen as the bleaching agent as it is mostly used by Indian paper industry because of economic reasons.

Results & Discussions

The initial brightness and yellowness of the unbleached pulps varied between 20-27% ISO (Brightness) and 51 to 63% (yellowness) due to variation in the raw material. Typical characteristics of one sample of unbleached pulp is shown in Table-1.

TABLE - 1

CHARACTERISTICS OF UNBLEACHED BAMBOO COLD SODA PULP

S.No.	Particulars	Unit	
1.	Kappa Number	–	158.00
2.	Brightness	% ISO	19.4
3.	Yellowness	%	53.8
4.	Ash	%	2.5
5.	Silica	%	1.2
6.	Solubility		
	a) Cold water	%	2.74
	b) N/10 NaOH	%	11.36
7.	Klason Lignin*	%	23.31
8.	Acid Soluble lignin	%	0.90
9.	Holocellulose	%	71.14
10.	Pentosans	%	15.60

* Corrected for ash.

TABLE - 2

EFFECT OF ALUM EXTRACTION ON PULP BLEACHABILITY

S.No.	Treatment Conditions	Bleahing Sequence	Brightness % ISO	Yellowness %
1.	—	Unbleached	24.6	62.3
2.	—	H2O	36.3	49.6
3.	Hot water 60ºC, 1 hr.	H2O	—	—
4.	3% Alum, 60ºC, 1 hr.	H2O	46.5	39.5
5.	—	H12H8	39.1	45.9
6.	3% alum, 40ºC, 1 hr.	H12H8	46.9	39.5

TABLE - 3

EFFECT IF SODIUM CARBONATE EXTRACTION ON PULP BLEACHABILITY

S.No.	Treatment Conditions	Bleaching Sequence	Brightness % ISO	Yellowness %
1.	—	Unbleached	27.2	55.0
2.	—	H10H12	46.6	40.5
3.	4% Na2CO3; 60ºC, 1 hr.	H10H12	49.6	38.0
4.	6% Na2CO3; 60ºC, 1 hr.	H10H12	51.4	37.4
5.	8% Na2CO3; 60ºC, 1 hr.	H10H12	50.7	37.9

It was thought that the high bleach consumption (hypochlorite bleaching) and poor bleachability be due to incrusting materials present in the pulp apart from the identified chomophoric groups. It is reported[10] that bamboo contains small amount of fine quality wax. The wax is possibly partially retained in the fibre creating a barrier to bleaching action. Furthermore, hypochlorite exerts oxidizing action on wax resulting in the formation of COOH and ester groups[11] of which the later is more difficult to remove. It is also possible, that some color bodies undergo photochemical polymerization[12 13] and are strongly adsorbed on the fibre surface[14]. So it was thought that removal of the incrusting materials from the pulp would possibly improve its bleachability. For this the unbleached pulp was pre-treated with various chemicals as shown in Table-2 and Table-3. Table 2&3 shows the effect of pulp extraction with alum and sodium carbonate prior to hypochlorite bleaching on pulp bleachability.

It is observed from Table 2 & 3 that pulp pre-extraction with alum and sodium carbonate are useful in improving pulp bleachability and reducing yellowness. However, alum was more effective than sodium carbonate.

As stated earlier carboxylic groups also contribute to pulp yellowing. Ionexchange reactions involving functional groups (carboxyl and phenolic -OH groups) associated with alpha and beta cellulose and lignin are possible and can be represented as follows:

$$2R.COOH + Mg.X_2 \rightleftharpoons (R.COO)_2 Mg + 2\,HX$$

where, R is a polysaccharide matrix and X is an acetate, chloride, hydroxide sulfate etc. anion. The monovalent cations are very mobile and possess relatively low affinity for organic functional groups. Trivalent and tetravalent cations although least mobile do not combine readily with these functional groups because of steric hindrance. The divalent cation appear to have the best affinity for carboxyl groups and diminished mobility. Bleaching studies were carried out after pre-treatment of the unbleached pulp with magnesium sulfate, barium hydroxide and barium chloride (Table 4). The results indicate that barium compounds are more effective than magnesium compounds. Comparision of results of Tables 2, 3 and 4 shows that pulp pre-treatment with alum is more effective than the other compounds.

TABLE - 4
EFFECT OF DIVALENT CATIONS ON BLEACHABILITY OF COLD SODA BAMBOO PULP

S.No.	Treatment Conditions	Bleaching Sequence	Brightness % ISO	Yellowness %
1.	—	Unbleached pulp	24.6	62.3
2.	—	H12H8	39.1	45.9
3.	$MgSO_4$ - 2%;40°C 2 hrs.	H12H8	43.7	42.6
4.	$Ba(OH)_2$-2%,40°C, 2 hrs.	H12H8	44.9	41.7
5.	$BaCl_2$-2%, 40°C 2 hrs.	H12H8	45.9	44.6

TABLE - 5
HYPOCHLORITE BLEACHING WITH SODIUM CARBONATE AS ADDITIVE

S.No.	Particulars	Brightness % ISO	Yellowness %
1.	Unbleached	27.2	55.0
2.	H10H12	46.6	40.5
3.	H10H12* (*4% Na_2CO_3)	53.8	34.6
4.	H10H12* (*5% Na_2CO_3)	53.5	34.5
5.	H10H12* (*6% Na_2CO_3)	54.8	34.6
6.	H10H15* (*15% Na_2CO_3)	56.4	31.5
7.	H10H8*H4** (*6% Na_2CO_3) (** 4% Na_2CO_3)	60.2	29.4
8.	H10H12*H3**(*6% Na_2CO_3) (**4% Na_2CO_3)	64.3	27.0

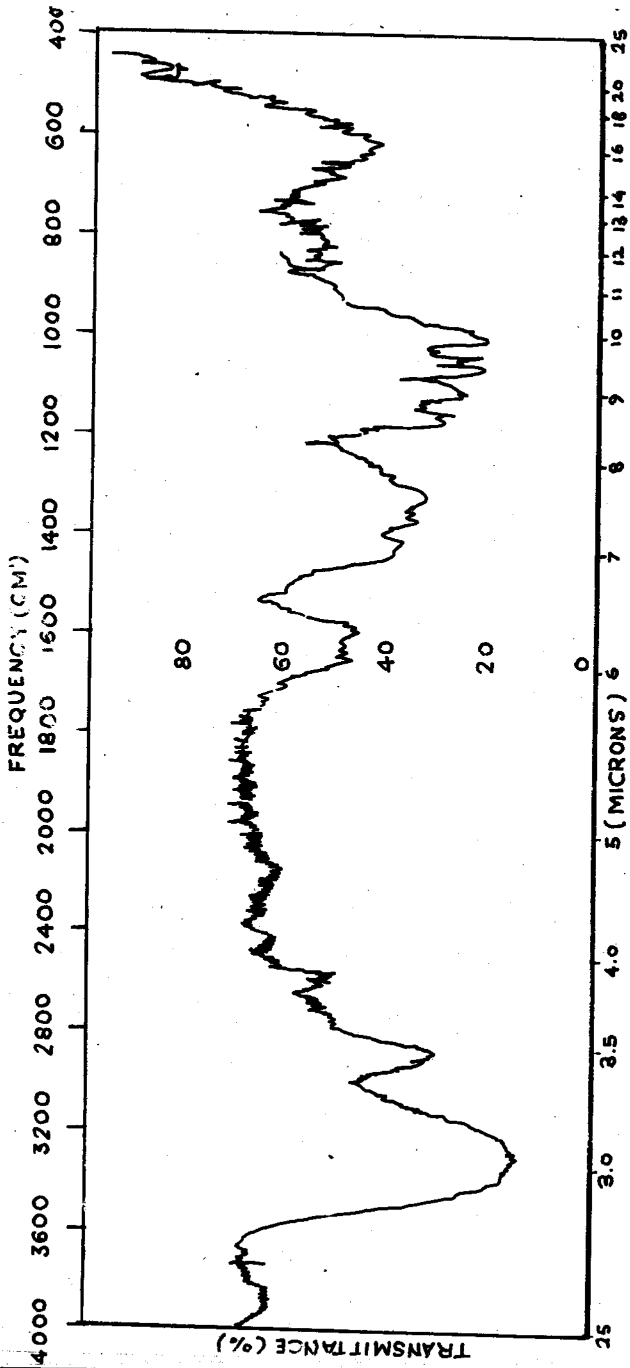


FIG. 1 I R SPECTRA OF THIN COLD SODA BLEACHED (With additive) PULP SHEET

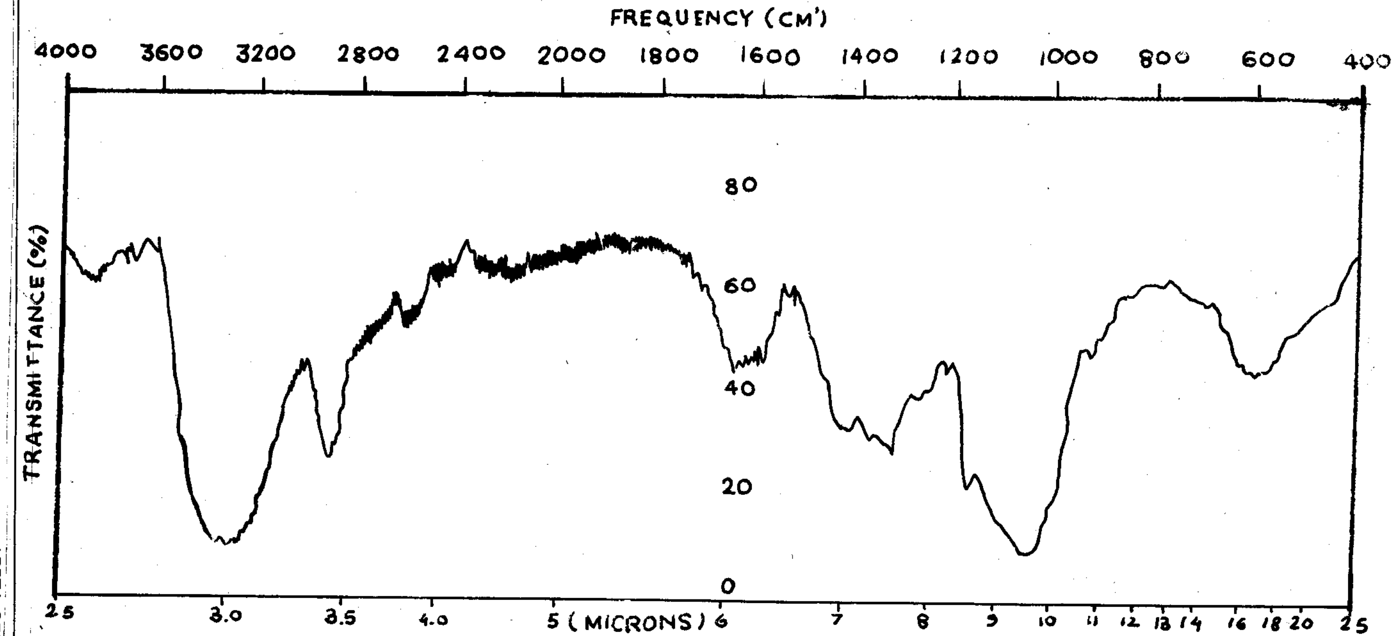


FIG. 2 I R SPECTRA OF THIN COLD SODA BLEACHED PULP SHEET

As mentioned earlier, pulp pre-treatment with sodium carbonate was found to be effective both in increasing brightness and reducing yellowness. Some experiments were carried using sodium carbonate as "additive" during hypochlorite bleaching. Small amount of caustic (approx. 2% on pulp) was added to maintain pH at around 9.5. Bleaching was carried out in two and three stages (H-H & H-H-H) while sodium carbonate was added in the second and third stages only. the results are shown in Table-5.

Comparision of results of Table 3 and Table-5 shows that addition of sodium carbonate during hypochlorite bleaching is more effective than pulp pre-treatment with it. It is also observed from Table-5 that even with the same amount of hypochlorite 5 to 8 points higher brightness and 4 to 5 points lower yellowness is obtained by bleaching in three stages (H-H-H) than bleaching in two stages.

IR Spectra of thin sheets of pulp bleached with and without sodium carbonate "additive" (Fig-1 and Fig-2 respectively) shows presence of much less carbonyl groups in the pulp bleached with sodium carbonate as additive. Reduction of carbonyl content and enhanced pulp bleachability is possibly due to direct production of nascent oxygen from excess free hypocholorous acid present in bleaching bath when sodium carbonate is used.

The possible mechanism of carbonyl reduction is as under:

During sodium carbonate "additive" bleaching the amount of caustic added as buffer is much less. During bleaching the pH dropped rapidly indicating depletion of caustic. In absence of excess alkali hypochlorite undergoes decomposition and liberates hypochlorous acid.

$$Ca(OCl2) + H2O \rightleftharpoons Ca(OH)2 + HCl$$

The unstable hypochlorous acid undergoes further rearrangements and produce nascent oxygen.

$$2\ HOCl \longrightarrow 2HCl + 2\ O \text{ (nascent oxygen)}$$

If excess alkali is present then part of HOCl reacts with alkali and produces free chlorine

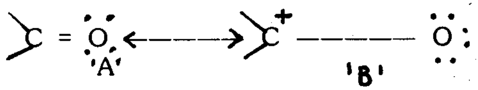
$$NaOH + HOCl \longrightarrow NaOCl + H2O$$
$$NaOCl + HCl \longrightarrow NaCl + Cl2 + H2O$$

Since hopochlorous acid does not react with weak bases like sodium carbonate, all the hypochlorous acid is converted to hydrochloric acid and nascent oxygen when sodium carbonate is present. The HCl is neutralised by Na2CO3 and produces carbon dioxide.

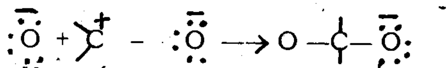
$$Na_2\,CO_3 + 2\ HCl \longrightarrow NaCl + H_2O + CO_2$$

Nascent oxygen being a strong oxidizing agent reacts with carbonyl group. The mechanism by which the nascent oxygen reacts with carbonyl group can be explained considering the polar structure of carbonyl group. Examination of electronic structure of carbonyl group shows that a carbon atom is bonded to a more electronegative oxygen. The resulting imbalance in the electron density leads to a permanent dipole for simple carbonyl compounds.

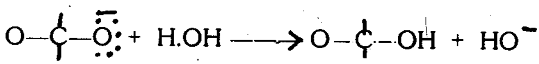
In resonance terms, the carbonyl group is represented by the two contributing structures A & B



Structure "B" indicates that carbon atom is electrophilic (electron-deficient) and can react with nucleophiles (electron rich) such as nascent oxygen.


(Nascent Oxygen) (unstable)

The reaction product is very unstable and the nucleophilic oxygen atom abstracts hydrogen atom from the solvent (water) to attain stable configuration.


(stable)

EXPERIMENTAL

Raw Material

Matured bamboo (4 yrs. old) collected locally having stored life of about 5/6 months after felling was used for the experiments. Bamboo was chipped into 2/3 cm length size and was screened to remove undersize and oversize materials.

Pulp Preparation:

Bomboo chips were soaked overnight at atmospheric pressure in caustic soda solution (25 gpl). Caustic added was 10% on o.d. chips. After impregnation excess liquor was drained and pulp was refined in laboratory. Sprout Waldron disc refiner. The unbleached pulp was screened before bleaching.

Bleaching

Bleaching was carried out in plastic bottles taking 20 gm o.d. unbleached pulp as per procedure outlined in reference (8).

IR Spectrophotometric Measurements

IR Spectra of pulps were recorded by preparing their thin sheets of 10 grammage[9] on P.E. Model 375 double beam spectrophotometer.

Conclusions

Cold soda bamboo high yield pulp has low initial brightnes and high yellowness and bleaching response of this pulp towards hypochlorite, dithionite, borohydride and hydrogen peroxide is very poor. Calcium hypochlorite bleachability of cold soda bamboo pulp is increased when the unbleached pulp is pre-treated with chemicals like alum, sodium carbonate, magnesium sulfate, barium chloride, barium hydroxide etc. However, better result is obtained using sodium carbonate as "aditive", during calcium hypochlorite bleaching. The enhanced bleachability is believed to be due to oxidation of carbonyl groups by nascent oxygen which is the active bleaching agent in sodium carbonate buffered calcium hypochlorite bleaching system.

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