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Bleaching of Cold Caustic Soda Pulps of Dendrocalamus Strictus And Mixed Hardwoods

The unbleached pulps of the bamboo and hardwoods obtained by cold caustic soda process possessed low initial brightness and consequently were hard to bleach. Different oxidative and reductive bleaching agents were tried for surface bleaching of the pulps. Straight hypochlorite bleaching required uneconomical quantity of the bleaching chemical to attain acceptable brightness. Single stage bleaching in normal practice with oxidative agents hypochlorite and peroxide could raise the brightness by about 10 points, whereas reducing bleaching agents, sulphite, hydrosulphite and borohydride could improve brightness by 2-4 points. Combination of bleaching sequences like H.P.; P.H., H.P.SO_3, P.P. hydro or P.P. borohydride were encouraging. Reducing agents in final stage of bleaching sequences could improve resistance to colour reversion. Trials for blending the cold soda wood pulps with sulphate bamboo pulp after alkali extraction before hypochlorite bleaching gave encouraging results. Having less binding properties there will be some limitation on the proportion of the cold soda pulps used in the blend.

The demand for more quantity of paper year after year and the need for developing new qualities in the paper have compelled pulp industrialists to investigate the possibility of utilisation of more and more varieties of fibrous raw materials available in nature and develop processes to suit the utilisation of these materials. Also obtaining higher and higher pulp yields has been the air to achieve economy as well as to meet the shortage in raw materials. This problem is no exception to India and the industry is trying to exploit the extensive hardwood forests to acquire its raw material requirement. In this direction the Andhra Pradesh Paper Mills at Rajahmundry, has put up a cold caustic soda semi chemical plant to augment its raw material requirement from the nearabout hardwood forests. The bleaching of the cold caustic soda pulp became a necessity to use them in various white and coloured varieties of utility papers. The manufacturing process of the pulp in the mill is described in an earlier paper (1).

The cold caustic soda process retains considerable amount of lignin in the pulp, the process being used only soften the chips to enable easy defibration. Because the fibre walls still contain lignin which inhibit fibre bonding in the paper making process, the pulps are used for such purposes as corrugating medium, cheap book and news-printing, sanitary and crepe papers etc where strength properties are not very important. Some of these papers require fairly high brightness and hence the pulp needs bleaching. The fairly white colour of the original wood gets reduced during cold caustic soda steeping process due to reaction with NaOH and further gets reduced during refining due to the high temperature attained at the interface between the fibre and the refiner discs. With temperate and cold climate hard woods the brightness of the cold caustic soda pulp is reported to be in the range of 35–55 per cent (2). But in the case of the Andhra hardwoods the brightness of the pulp were found to fall down to 23–26 per cent.

The cold soda pulps are essentially chemimechanical pulps and the bleaching procedures developed for N.S.S.C. and groundwood involving one or more stages of hypochlorite, peroxides or hydrosulphites in various combinations can be applied to these pulps also (3). Brightening results of 55–75 per cent could be obtained with pulp strength unchanged or slightly increased. Brit (4) observes that only slight loss in yield and improvement in strength result in single stage hypo bleaching of such pulps. Rydholm (2) gives instances of bleaching eucalyptus, birch aspen and poplar pulps having 35–55 per cent brightness to 65–70 per cent using 100–150 kg ptp active chlorine as hypochlorite in stages. The same effect is reported to occur by bleaching with 1-2 per cent peroxide. Simmond (6) opines that hardwood pulps can be brightened using reasonable amount of chlorine as hypochlorite. He has reported using 10% chlorine as hypochlorite and sodium hydroxide and silicate buffers the hardwood pulps could be bleached upto 70% brightness. R.V. Bhat and P.R. Gupta (7) have reported bleaching of cold caustic soda pulp of eucalyptus globulus

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having unbleached pulp brightness 45% to 56% using 10% bleaching powder. S.R.D. Guha *et al* (8) and G.M. Mathur *et al* (9) also have obtained 68–74% brightness by bleaching cold soda pulps of eucalyptus grandis with 7.5% calcium hypochlorite.

Whereas with straight hypochlorite bleaching pulps are brightened with insignificant yield loss, higher brightness can be obtained with multistage bleaching using chlorination, alkali extraction and hypochlorite (CEH) sequence. This also improves the strength properties of the pulps. But such a sequence affects the pulp yield adversely. Casey (10) has reported a yield loss from 75 to 60% when bleaching N.S.S.C. pulps to 80–87% brightness.

Considerable literature is available on the lignin preservative bleaching of high yield pulps using oxidative and reducing bleaching agents, namely sodium and hydrogen peroxides, sodium and zinc hydrosulphites, sodium bisulphite, sodium sulphite and sodium borohydride. Out of all these agents peroxides and hydrosulphites are universally being used. The remaining bleaching agents have the limitations of either high cost or low efficiency. These bleaching agents are either used individually or in combination. Casey (10) and Rydholm inform that additive results are obtained by conducting two-stage bleaching with peroxide followed by hydrosulphites when brightness value can increase by 18–35 points. The speciality of these bleaching agents is their ability to decolorise only the chromophoric groups without seriously affecting the pulp yields which are reported to be 96–100% of the unbleached pulp (2, 11).

Various aspects of bleaching are studied. These are consistency, temperature, reaction time, buffering and chelating agents. Simmonds *etal* (11) report optimum alkalinity of 2–3·6% Na_2O during peroxide bleaching. Above this the rate of reaction increases. But the brightness gain is lowered due to reduced stability of the peroxide. They also state that the stability of the peroxide bleached pulps is higher than those of the hypochlorite bleached ones. In the final stage after hypo or peroxide bleaching, it is reported treatment with sulphurous acid improves resistance of pulp to colour reversion as well as brightness by one or two points. Bayer (12) states that brightness improvement depends on the type of pulp also in addition to other process variables. He reports brightness increase in mill trials from 60–69 to 75% using 1–3% peroxide. The advantages of peroxide bleaching is cited as increase in brightness, improved sheet formation, improved drainage on wire, dirt removal, increased softness, less loss of brightness in dryers, tensile strength, burst and bulk are unchanged.

Brit (4) has reported improvement in brightness upto 80% when unbleached cold soda pulps with 30–40% were refiner bleached and further treated with two-stage peroxide-hydrosulphite. Rydholm (5) states that brightness increase upto 35 points can be obtained using two-stage peroxide 2–3% Na_2O_2 and hydrosulphite (1% $Z_nS_2O_4$) bleaching. Yankowski (13) reports additive results leading to 80% brightness when ground wood pulp was bleached in two stages using hypochlorite or peroxide and then with hydrosulphite. Sodium or Zinc hydrosulphites are commonly used for bleaching ground wood pulps having high initial brightness. These as well as sodium tetraborohydride are reported to give brightness increase upto 20 points when 2% of them are used on pulp. Sodium sulphite and bisulphites are also some times used. But their brightness improving power is low (1–3 points) when used upto 3%. However, they are some times used in the final stage after oxidative bleaching with hypochlorite or peroxide.

Theories of bleaching:

The coloring phenomena in the unbleached pulp is associated with the carbonyl, p-hydroxy phenyl, quinone and adjacent carbonyl groups of the degradation products of lignin or carbohydrates which are absorbed on the pulp. The colour developed in the visible spectra is due to the electron transition from the ground state to an excited state of a molecule. The bleaching process eliminates mobile electrons in the chromophoric system as a result of reaction or rupture of the conjugated double bonds. The active compounds in the bleaching agents are either nascent hydrogen or oxydants containing highly electronegative elements.

Some discussion of the reaction of these compounds is briefly given here:

C E H sequence:

Chlorine in an aquaous solution undergoes the following equilibrium

$$Cl_2 + H_2O_2 \rightleftharpoons H^+ + Cl^- + HOCl$$

The weak hypochlorous acid further dissociates as follows:

$$HOCl \rightleftharpoons H^+ + OCl^-$$

The relative concentrations of the different molecules and ions depend upon the hydrogen ion concentration. Molecular chlorine is the main constituent below pH 2. Between 2 and 4 pH chlorine and non-ionised hypochlorous acid exist. Between 4 and 6 pH weakly ionised HOCl predominates. Between 6 and 8 pH there is mixture of HOCl and fully ionised HOCl. Above 9 pH only the ionised hypochlorite exists.

Elemental chlorine acts with lignin mainly by substitution and partly by addition. The products of reaction are partly soluble in water and most of them removed in the alkali extraction.

Hypochlorite bleaching

Above 9 pH the reaction of hypochlorite is oxidative, the control of pH and bleaching becomes easy. With low alkalinity the pH of the pulp system further falls down, due to reactions, to the range when HOCl appears. Brightness increase will be low. At higher alkalinity reaction rate is decreased and brightness increased. The control of pH is attained by the addition of caustic soda or sodium silicate which act as buffers. Consistency, reaction, temperature and time are important variables in hypochlorite bleaching. At consistencies above 10% the reaction rate becomes so rapid that it will be difficult to control. Temperature much above 40°C should not be used to avoid too much of degradation.

Peroxide and reductive bleaching agents:

Peroxides act on the colouring matter but do not cause appreciable change in lignin or carbohydrates. The peroxide on ionisation form HO_2 ions which are considered as the active bleaching agent. The equilibrium existing in the system may be represented as follows:

$$H_2O_2 + OH^- \rightarrow OOH^- + H_2O$$

The presence of an alkali promotes the formation and stabilisation of the hydroperoxide ion. In acid medium H_2O_2 decomposes to oxygen and escapes without affecting the pulp. For maximum efficiency, the pH of the system at 10–10.5 is desirable. The peroxides Na_2O_2 and H_2O_2 are unstable due to the catalyting effects of traces of heavy metal ions like copper, mangnese, chromium etc. or enzymes such as catalyse (3–12, 13, 14) produced by biological activity. Hence, for maximum efficiency these are to be removed or otherwise they impair the brightness by direct discoloration of the pulp or acting as decomposing catalysts. The inactivation of the catalysers is caused by either absorption or complexing with certain additives. The inactivation of the catalysts is attained by the use of some compounds such as sodium silicate or stannate, $MgSO_4$ or sodium pyroposphates. Also certain chelating agents like Tetrasodium salt of E.D.T.A. Penta sodium salt of DTPA are used. These compounds function either as absorbents or complexing agents. For removal of the catalysing substances some authorities have suggested pretreatment of pulp with chlorine, calcium chloride or sulphuric acid (2) to dissolve out the heavy metals. Pretreatment with $CaCl_2$ is found to increase brightness by1 -2 points.

Ground wood pulps are quite often bleached with reducing agents, namely zinc and sodium hydrosulphites. These reducing agents are supposed to add hydrogen to the unsaturation in the chromophoric groups in the colour constituents and reduce them colourless. These agents have some drawback of increasing corrosion in the system. The reducing action of the hydrosulphites is supposed to take place as per the following equation—

$$Na_2S_2O_4 + 4H_2O \rightarrow 2NaHSO_4 + 6H$$

But hydrosulphites can decompose according to one of the following reactions—

(i) $2Na_2S_2O_4 \rightarrow Na_2S_2O_3 + Na_2S_2O_5$

(ii) $2Na_2S_2O_4 + H_2O \rightarrow Na_2S_2O_3 + 2NaHSO_3$

These reactions can be reduced by the addition of sequestering agents like polyphosphates, E.D.T.A. etc.

Borohydrides of sodium and potassium have got high reducing potential since they can give 8 equivalents of hydrogen as per the following equation—

$$NaBH_4 + 2NaOH + H_2O \rightarrow Na_3BO_3 + 4H_2$$

The action of the borohydrides is the reduction of the carbonyl groups to alcohol groups and increase brightness stability.

EXPERIMENTAL

Pulps:

Bleaching studies were made on cold caustic semichemical pulps of mixed hardwoods and medar bamboo (dendrocalamus strictus). These woods obtained from nearabout forest, were sound and stored for a period of about four months. For our experiments woods were mixed in equal proportion and cold soda semichemical pulp was prepared in the plant. The process in essence consists of cooking of splinters of wood in solution of caustic soda at 30°C–45°C for about 2 hours, then refining in two stages in the Sprout Waldron disc refiners. The wood chips before treatment were having brightness of about 50–55%. The brightness of the refined pulp was found to be 25% in the case of woods and 23% in the case of bamboo. The Kappa numbers of the pulps were 115 and 120 respectively.

Some experiments were conducted using blends of cold soda wood pulp and alkali extracted bamboo sulphate chemical pulp. The permaganate number of the unbleached bamboo chemical pulp was 28 and that of alkali extracted pulp 12.

Bleaching chemicals:

1. Chlorine emulsion—prepared in the laboratory by passing chlorine gas in water. The concentration of the emulsion was about 5 gpl.
2. Calcium hypochlorite—solution prepared in the mill by passing

chlorine in milk of lime in a reactor.

3. Caustic soda—commercial grade of 99% purity.
4. Sodium silicate—commercial grade with $Na_2O:SiO_2$ ratio 1:2.4.
5. Sodium sulphite—commercial grade of 86% purity.
6. Other chemicals, magnesium sulphate, ethylenediamine tetra acetic acid, hydrogen peroxide, sodium borohydride, sodium hydrosulphite, and sulphuric acid were all of chemically pure laboratory grade.

Bleaching:

Bleaching experiments were conducted in the laboratory using pulp equivalent to 50 gr. oven dry. The wet laps were squeezed to about 28% dry content and then stored in a polyethene bag to equilibrate for moisture for atleast four hours. Duplicate samples were kept for moisture determination.

Bleaching experiments were conducted in plolyethene bottles with screwed caps. The bottles were kept in a larger vessel containing water. The temperature of the contents of the bottles were maintained by adjusting the temperature of water in the bath. During the reaction period the contents of the bottles were mixed intermittently by shaking the bottles well. The pH of the pulp was tested from time to time in an electronic instrument and adjusted at the required level by adding suitable reagent such as NaOH or sulphuric acid.

After the reaction was over the pulp was transferred on a buchner funnel, the filtrate was recirculated till free of fibres. The pulp was then washed with warm distilled water about 50°C, till free of chemicals and colouring of matter.

The pulp was then squeezed and conditioned as mentioned earlier and samples were kept in the oven at 105°C for yield determination. Brightness values were determined on pulps sheets prepared on a buchner funnel, pressed and dried as per the TAPPI standards procedure. Brightness was tested in an elrepho brightness tester.

METHODS OF BLEACHING

(1) C.E.H. sequence:

The cold caustic semichemical pulps of both bamboo and the hard woods were highly ligninous and coloured and seemed to be difficult to bleach since the initial brightness of the unbleached pulps was found to be as low as 23 and 25 respectively. Various bleaching methods were tried to study the effects on yields and the efficacy of the methods to improve the brightness of the pulps. Our idea was to attain a reasonable brightness above 65% so that the pulps could be blended with bleached chemical pulps. To do so some experiments were conducted to find out whether the conventional CEH sequence will yield sufficiently bright pulps even with some loss of yields. The bleaching conditions, the brightness and yield values are given in table I. The brightness gain even with a heavy yield loss was very insignificant, i.e., only 31 and 35 respectively.

TABLE 1

BLEACHING OF COLD CAUSTIC SODA SEMI-CHEMICAL PULP CEHH SEQUENCE:

Chlorination		**Hard wood**	**Bamboo**
Cl_2 added	%	10	12
Consistency	%	3	3
Temperature	°C	28	28
Time	Minutes	60	45
Cl_2 consumption	%	10	11.5
Alkali extraction:			
NaOH added	%	5	3
Consistency	%	8	8
Temperature	°C	60	60
Time	Minutes	120	120
NaOH consumption	%	5	3
Hypochlorite stage:			
Cl_2 added	%	8	8
Consistency	%		8
Temperature	°C	45	45
Time	Minutes	90	90
pH		8.5–9.0	8.5–9.5
Cl_2 consumed	%	10	8
Total Cl_2 consumed	%	20	19.5
Brightness	%		
Unbleached pulp	%	23.5	23.0
Bleached pulp		35.0	31.0
Yield on unbleached pulp,	%	81.0	80.0

(2) Some experiments were conducted to study the effect of straight hypochlorite bleaching on the cold soda pulps. The pulps were treated with different quantities of calcium hypochlorite. In order to study to what extent brightness value can be obtained, chlorine as hypochlorite upto 50% on the basis of pulp was applied. During reaction, sodium hydroxide was added as the buffer to maintain pH. The bleaching conditions and results are given in table 2.

(3) Some experiments were conducted to study the effect of hypochlorite bleaching of the cold soda wood pulps along with the alkali extracted bamboo pulp. The idea was to see if the cold soda pulp can blend well with bamboo pulp in mixed bleaching without giving any heterogenity like mottling to the final pulp mixture. The alkali extracted bamboo pulp was mixed with different quantities of cold soda wood pulp and bleached with varying quantities of calcium hypochlorite corresponding to the increased quantity of wood pulp used. Bleaching conditions were used suitable to be employed in the conditions of the plant. The bleaching conditions and brightness results are given in tables 3A and 3B.

TABLE 3A

HYPOCHLORITE BLEACHING OF MIXED PULPS

1. Bamboo chemical pulp after alkali extraction at the plant.
2. Cold caustic soda semi-chemical pulp from hard woods.

A. Bleaching condition at the plant:

CHLORINATION		
Consistency	%	3.0
Temperature	°C	30
Time	Hours	1.0
Cl_2 consumption	%	10.0
Alkali extraction:		
Consistency	%	8.0
Temperature	°C	60.0
pH		8.5–9.5
Time	Hours	2.5
Alkali consumption	%	3.9

TABLE 2

HYPOCHLORITE BLEACHING

	Hard woods				Bamboo		
	1	2	3	4	1	2	3
Consistency, %	10.0	10.0	10.0	10.0	8	12.0	8.0
Reaction time, mts	120	120	120	120	150	150	150
Temperature °C	43±1	43±1	43±1	43±1	43±1	43±1	43±1
pH	8.5–9.5	8.5–9.5	8.5–9.5	8.5–9.5	8.5–9.5	8.5–9.5	8.5 9.5
NaOH consumption as buffer %	2.0	2.6	3.8	6.4	—	2.5	2.8
Hypochlorite added as Cl_2 %	12.0	18.0	30.0	50.0	8.0	18.0	21.0
Chlorine conumption, %	12.0	18.0	30.0		8.0	18.0	21.0
Brightness of unbleached pulp, %	25.0	25.0	25.0	25.0	23.0	23.0	23.0
Brightness of bleached pulp %	32.0	35.0	56.0	69.0	31.0	32.5	33.0
Bleached pulp yield on unbleached pulp %	97.2	97.0	96.4	93.3	98.0	97.0	97.0

TABLE NO. 4A

STRENGTH PROPERTIES OF BAMBOO AND MIXED COLD CAUSTIC SEMI-CHEMICAL PULP

A. 30° SR		100% bamboo wood	90% bamboo 10% wood	bamboo 20% wood	70% bamboo 30% wood
Basis weight	g/m²	61.5	60.8	61.7	59.6
Tensile strength	kg/cm	3.39	1.00	1.63	1.56
Breaking length	metres	5500	3290	2650	2620
Bursting strength	kg/cm²	2.20	1.30	1.10	1.05
Burst factor		36.0	21.0	19	18
Folding endurance, No. of double folds		40	8	6	5
B. 40° SR					
Basis weight	g/m²	60.9	61.2	61.3	60.0
Tensile strength	kg/cm²	3.65	2.50	1.75	1.60
Breaking length	metres	6000	4080	2870	2670
Bursting strength	kg/cm²	2.5	1.52	1.18	1.05
Burst factor		41	25	19	18
Folding endurance No. of double folds		61	15	7	6

TABLE 3 B

HYPOCHLORITE BLEACHING

		100% bamboo	90%bamboo 10% wood	80% bamboo 20% wood	70% bamboo 30% wood	100% bamboo cold caustic	100% hard wood cold caustic	Remark
Consistency	%	8	8	8	8	8	8	In these cases the % chlorine consumed at chlorination stage was 10%
Temperature	°C	45	45	45	45	45	45	
pH		8.0-10	8.0-10	8.0-10	8.0-10	8.5-9.5	8.5-9.0	
Time	Hrs	3	4	4	4	1.5	1.5	
Cl_2 consumption		4.9	6.5	7.5	9.0	8.0	12	
NaOH consumption as buffer		1.6	1.8	3.0	3.9	—	—	
Brightness	%	77.5	71.0	69	60	31.0	32	
Yield % (on alkali extracted/and unbleached cold caustic pulp		96.8	96.8	95.6	96.6	98.0	98.0	

The bleached pulps were beaten in the laboratory valley beater to 30 and 40°SR values and standard sheets were prepared in the Lhomargy French standard Sheet Former. The sheets were pressed, dried and conditioned as per TAPPI standard and tested for strength properties which are shown in table 4A.

Some experiments were also conducted to find out the effect of blending of the peroxide bleached wood pulp with bleached bamboo chemical pulp both of which were separately beaten and then mixed. Standard sheets were made and tested for strength properties, the values are given in table 4B.

(4) The hypochlorite bleaching of cold soda pulps of both bamboo and woods, within practical limits could not increase the brightness above 35%. Hence other methods of bleaching were tried separately and in combination in different stages. Hydrogen peroxide, very commonly used for semichemical pulps, was tried along with the chelating and stabilising agents as per standard practice. It was found with cold

TABLE NO. 4B

STRENGTH PROPERTIES OF BLEACHED KRAFT BAMBOO PULP AND PEROXIDE BLEACHED COLD SODA WOOD PULP BLENDS (SEPARATELY BEATEN AND MIXED)

		100% B	90% B 10% Co	80% B 20%Co	70% B 30% Co	60% B 40% Co
Freeness 30° SR						
Properties:						
Basis wt.	gsm	59.5	61.3	60.5	61.0	60.3
Bursting strength	kgs/cm²	1.6	1.25	1.2	0.95	0.75
Burst factor		27	20	20	16	12
Tensile strength	kgs/cm²	2.28	2.2	1.56	1.33	1.33
Breaking length	metres	3820	3590	2580	2180	2210
Double folds		7	3	2	2	1
Freeness 40° SR						
Basis wt.	gsm	60.5	61.0	60.8	60.8	60.2
Bursting strength	kgs/cm²	1.75	1.3	1.1	1.0	0.85
Burst factor		29	21	17	15	14
Tensile strength	kgs/1cm²	2.38	2.27	1.87	1.53	1.4
Breaking length	metres	3950	3640	3150	2520	2330
Double folds		9	5	4	4	3

soda wood pulp that when only peroxide was used as the bleaching agent in two stages, though there was considerable brightness increase from 25% to 42%, this was not sufficient to utilise the pulp for printing grade papers. Hence to achieve higher brightness, the pulps were first bleached with 18% chlorine as calcium hypochlorite in single stage, washed and then treated with hydrogen peroxide. Before the addition of hydrogen peroxide the pulps were treated with chelating and stabilising agents ethylene diamine tetra acetic acid and magnesium sulphate and sodium silicate were added as stabiliser and buffer to maintain pH during reaction.

One experiment was conducted to see if C E H pre-treatment to the pulp has beneficial effect compared with only hypochlorite treatment before peroxide bleaching. The bleaching conditions and results are given in table 5.

(5) Some experiments were conducted to find out the feasibility of using the cold soda wood pulps with bamboo pulp in the normal course of bleaching at the plant and at the same time obtain acceptable brightness, above 70%. The idea was to bleach the semichemical pulps partly with hydrogen peroxide in the cold soda section of the plant where the bleaching action could be carried out inside the storage tanks. The pulp after washing could further be sent to the hypochlorite bleaching towers to be mixed with the alkali extracted bamboo sulphate pulp. The effect of hypochlorite bleaching on the cold soda pulps which were pre-bleached with H_2O_2 is shown in table 6.

To study the effect of hypochlorite bleaching along with alkali extracted bamboo pulp, the semi-chemical wood pulps were treated with 1.5% H_2O_2 and then 10–20% of this washed pulp were mixed with 90–80% of

TABLE NO. 5

PEROXIDE BLEACHING

Chlorination:				
Cl_2 added	%	6		
Consistency	%	3		
Temperature	°C	29		
Time	Minutes	60		
Alkali Extraction:				
NaOH added	%	4		
Hypochlorite addedas Cl_2	%	8		
Consistency	%	8		
Temperature	°C	60		
Time	Minutes	120		
Hypo		**Bamboo**	**Bamboo**	**Hard woods**
Cl_2	%	4	18	18
Consistency	%	8	12	10
Temperature	°C	45	45	45
Time	Minutes	120	120	120
Total Cl_2 consumption	%	12	18	18
Brightness	%	29	33	35
Peroxide:				
H_2O_2	%	1.5	1.5	1.5
Consistency		10	12	10
E. d. t. a.		0.05	0.05	0.05
Mg SO_4		0.05	5.0	5.0
Na^2 SiO_3		5.0	5.0	5.0
Temperature	°C	70	70	70
Time	Hours	2.0	2.0	2.0
pH		9-10	9-10	9-10
Brightness	%	39.5	54.5	57.0
Yield	%	86.0	97.0	96.8

chlorinated and alkali extracted bamboo sulphate pulp obtained from the plant. This pulp mixture was further bleached with different quantities of calcium hypochlorite for two hours at 8% consistency and 43°C. The pulp was washed and then given a final sodium sulphite treatment at about 3 pH for improving brightness and resistance to colour reversion.

The components of the pulp mixtures, chemical consumption and brightness values are given in table 7. To confirm the results, another set of experiments was done on similar lines, but with the exception that all stages of bleaching including chlorination and alkali extraction of the bamboo sulphate pulp were wholly done in the laboratory. The results

TABLE NO. 6

PEROXIDE—HYPO BLEACHING

Peroxide stage		1	2
Consistency	%	10	10
Time	Mts	60	60
Temperature	°C	70	70
pH		9.5–10.5	9.5–10.5
$Na_2Si_2O_3$	%	5.0	5.0
$MgSO_4$	%	0.05	0.05
Edta	%	0.05	0.05
H_2O_2	%	1.5	1.5
Hypo			
Consistency	%	10	10
Time	Mts	120	120
Temperature	°C	45	45
pH		8.5–9.5	8.5–9.5
Alkali added as buffer	%	2.4	3.6
Hypo	%	8	18
Brightness	%	50	63
Yield	%	96.8	95.0

TABLE 8

BLEACHING CONDITIONS

1 Peroxide:		
Pretreatment and conditions as shown in table 6.		
2 Sodium sulphite:		
Consistency	%	5.0
Temperature	°C	60+2
Time of reaction	Minutes	30
pH during reaction (by adding H_2SO_4)		2.5–3.0
3 Sodium Hydrosulphite:		
Sodium hexametaphosphate,	%	0.5
Edta	%	0.05
Consistency	%	8.0
Temperature	°C	60+2
Time	Minutes	60
pH during reaction		5.5–6.0
4 Borohydride:		
Consistency	%	6.0
Edta	%	0.05
Temperature	°C	60
Time	Minutes	180
pH		9.0–9.5

TABLE No. 7

HYPOCHLORITE BLEACHING OF PEROXIDE TREATED COLD SODA WOOD PULP WITH ALKALI EXTRACTED BAMBOO SULPHATE PULP

Sl. No.	Bamboo chemical pulp %	Wood semi-chemical pulp %	Chlorination C 12 %		Alkali Extr NaOH		Peroxide on pulp %	Sulphite on pulp %	Hypo-chlorite C 12 %	Brightness GE %	Remarks
			Bamboo	Wood	Bamboo	Wood					
1.	100	0	10	—	4	—	—	—	5.0	78	
2.	0	100	—	10	4	—	—	—	10.0	35	
3.	0	100	—	—	—	—	—	—	18.0	35	
4.	90	10	10	—	4	—	1.5	1.0	7.0	70	
5.	90	10	10	—	4	—	—	—	7.0	67	
6.	80	20	10	—	4	—	1.5	1.0	8.0	70	
7.	80	20	10	—	4	—	—	—	8.0	69	
8.	100	—	10	—	3	—	—	—	5.0	74	Bamboo pulp bleached in lab. by CEHH
9.	80	20	10	—	3	—	1.5	1.0	8.0	70	
10.	80	20	10	—	3	—	—	—	8.0	64	

of these experiments also are given in table No. 7.

(6) Some experiments were conducted to study the effect of the reducing bleaching agents on the cold soda wood pulps. The pulps were treated with the necessary chelating agents before applying the chemicals. The conditions of bleaching were selected such that the same are most commonly applied and can be practical to be used on a commercial scale

TABLE 9

BLEACHING WITH DIFFERENT CHEMICAL AND SEQUENCES

S.No.	Sequence	Chemicals %						Yield %	Brightness %
1.	Hypochlorite (H)	Chlorine as Calcium hypochlorite	: 18.0	—		—		97.0	35
2.	Peroxide (P)	H_2O_2	: 1.5	—		—		97.6	35
2a.	P.P.	H_2O_2	: 1.5	H_2O_2	: 1.0	—		97.5	42.0
3.	Hydrosulphite (Hydro)	$Na_2S_2O_4$	: 1.0	—	—	—		97.6	28.5
4.	Borohydride (Boro)	$NaBH_4$	: 0.5	—	—	—		96.7	28.5
5.	Sodium sulphite (Sulphite)	Na_2SO_3	: 2.0	—		—		98.5	27.5
6.	H.P. Sulphite	Hypo as Cl_2	: 18	H_2O_2	: 1.5	Na_2SO_3	: 1.0	96.0	61.0
7.	P. Sulphite	H_2O_2	: 1.5	—		Na_2SO_3	: 1.0	97.5	37.0
8.	P. P. Sulphite	H_2O_2	: 1.0	H_2O_2	: 1.0	Na_2SO_3	: 0.75	97.5	45.0
9.	P. P. Hydro	H_2O_2	: 1.5	H_2O_2	: 1.0	$Na_2S_2O_4$	: 1.0	97.6	50.0
10.	P. P. Boro	H_2O_2	: 1.5	H_2O_2	: 1.0	$NaBH_4$	: 0.5	97.6	50.0

when the required chemicals become available at cheaper rates. Some experiments were also tried to study the effect of combination of bleaching after peroxide treatment since the brightness values obtained only with the reducing agents were found to be low. In each stage of bleaching the pulp was washed free of the previous chemical. The conditions of bleaching and the brightness results are given in tables 8 and 9.

To study the resistance of bleached pulp to colour reversion the air dry sheets were kept in a hot air oven at 105°C for a period of one hour and the reduction in the brightness observed. The post colour numbers were then calculated which are given in table 10.

The proximate chemical analysis of the different woods, bamboo and the semichemical pulps were done according to TAPPI standard methods and the same are given in table No. 12. The botanical names of the wood species are also given in the same table.

TABLE 10

BRIGHTNESS REVERSION OF COLD SODA WOOD PULP, BAMBOO KRAFT PULP AND POST COLOUR NUMBER

	Bleaching sequence	Original brightness %—R1	Brightness after keeping at 105° C for 1 hour — R2	Post colour number
1.	P	35	34	2.5
2.	P-P Sulphite	45	42	6.42
3.	H-H	56	49	9.30
4.	H-P	57	52	5.93
5.	H-P Sulphite	61	57	3.75
6.	CEH Bamboo kraft	77	63	7.42
7.	P-BH_4	50	48	3.14
8.	P-Hydro	50	48	3.14
9.	CEH.	35	33	7.7

Discussion of results

Table 1 shows that multistage bleaching of cold soda pulps of both mixed hard woods and dendrocalamus strictus by C E H sequence does not give appreciable brightness even with 20% chlorine consumption. The final brightness was 31 and 35% respectively. The pulp being highly lignino us the yield loss was quite high, that is, of the order of 20% on unbleached pulp. Bleaching cost will be quite high considering the heavy capital investment on the plant and the expenses of the chemical and operations.

Table 2 gives the results of bleaching the woods and bamboo by single stage hypochlorite bleaching, with different amounts of bleaching agent. A study of the table shows that the bleachability of the hardwood pulps is better than that of the bamboo pulps. However, even for the wood pulps it will not be economical since, to attain reasonable brightness large quantity of hypochlorite is required. The yield losses are not high. The purpose of this bleaching was to study the effect of hypochlorite bleaching on the cold soda wood pulp when mixed with bamboo pulp after alkali extraction. The trend of brightness increase and yield decrease with increased amounts of hypochlorite is shown in fig. 1.

Table No. 3 shows the effect of bleaching of the wood pulps with hypochlorite in mixture with the bamboo pulp after alkali extraction, since this was the most practical way of bleaching under the existing circumstances. Different quantities of wood pulps were used in the mixture and bleaching chemical was increased successively according to the percentage of wood pulp. The results show that combined bleaching is possible upto the extent of 20% of wood pulp in the mixture. Higher than this quantity adversely affects the brightness as also the economics of the process due to high bleach consumption. The bleach consump-

TABLE NO. 11

COST OF BLEACHING OF COLD SODA WOOD PULP

Sequence No.	Bleaching sequence	Chemical used	%	Brightness %	Bleaching cost for 100 tons pulp Rs.
1.	SULPHITE	Sodium Sulphide	2.0	27.5	3,740
2.	BOROHYDRIDE	Sodium borohydride	0.5	28.5	7,750
3.	HYPOCHLORITE	Calcium Hypochlorite as chlorine	12.0	32.0	1,33,20
4.	HYPOCHLORITE	—do—	18.0	35.0	19,430
5.	PEROXIDE+ SULPHITE	Hydrogen Peroxide Sodium Sulphite	1.5 1.0	37.0	26,460
6.	PEROXIDE+ PEROXIDE	Hydrogen peroxide	2.5	42.0	35,600
7.	PEROXIDE+ SULPHITE	Hydrogen Peroxide Sodium Sulphite	2.5 0.75	45.0	37,300
8.	PEROXIDE+ BOROHYDRIDE	Hydrogen Peroxide Sodium borohydride	2.5 0.5	50.0	43,350
9.	HYPOCHLORITE+ PEROXIDE	Hypochlorite Hydrogen Peroxide	18.0 1.5	57.0	43,780
10.	HYPOCHLORITE+ PEROXIDE+ SULPHITE	Hypo- Peroxide Sodium Sulphite	18.0 1.5 1.0	61.0	45,890
11.	PEROXIDE+ HYPOCHLORITE	Peroxide Hypochlorite	1.5 18	63.0	43,780

TABLE 12

		Casurina	Magnifolia medica	Adina eardifolia	Bombax mulberica	Boswellia serrata	Zenia grandis	Bamboo Dendrocalamus strictus	Cold soda pulps	
									Bamboo	Wood
Ash	%	0.76	0.47	0.45	0.83	1.03	2.35	3.98	3.85	2.00
Silica	%	0.36	0.23	0.22	0.35	—	—	2.00	—	—
1% NaOH solubility	%	16.50	17.70	16.00	13.60	15.50	19.50	23.00	17.70	16.34
Cold water solubility	%	3.77	2.85	5.82	2.70	4.88	2.60	5.70	3.13	3.25
Hot water solubility	%	4.85	4.81	8.17	3.58	6.71	2.84	6.90	5.60	6.37
Alcohol B solubility	%	3.45	2.51	4.48	4.31	3.70	5.10	2.20	3.24	2.52
Lignin	%	25.30	22.40	29.50	31.00	24.30	26.70	24.90	24.90	29.30
Pentosans	%	16.20	15.10	11.50	12.40	15.80	12.10	16.70	15.50	16.70

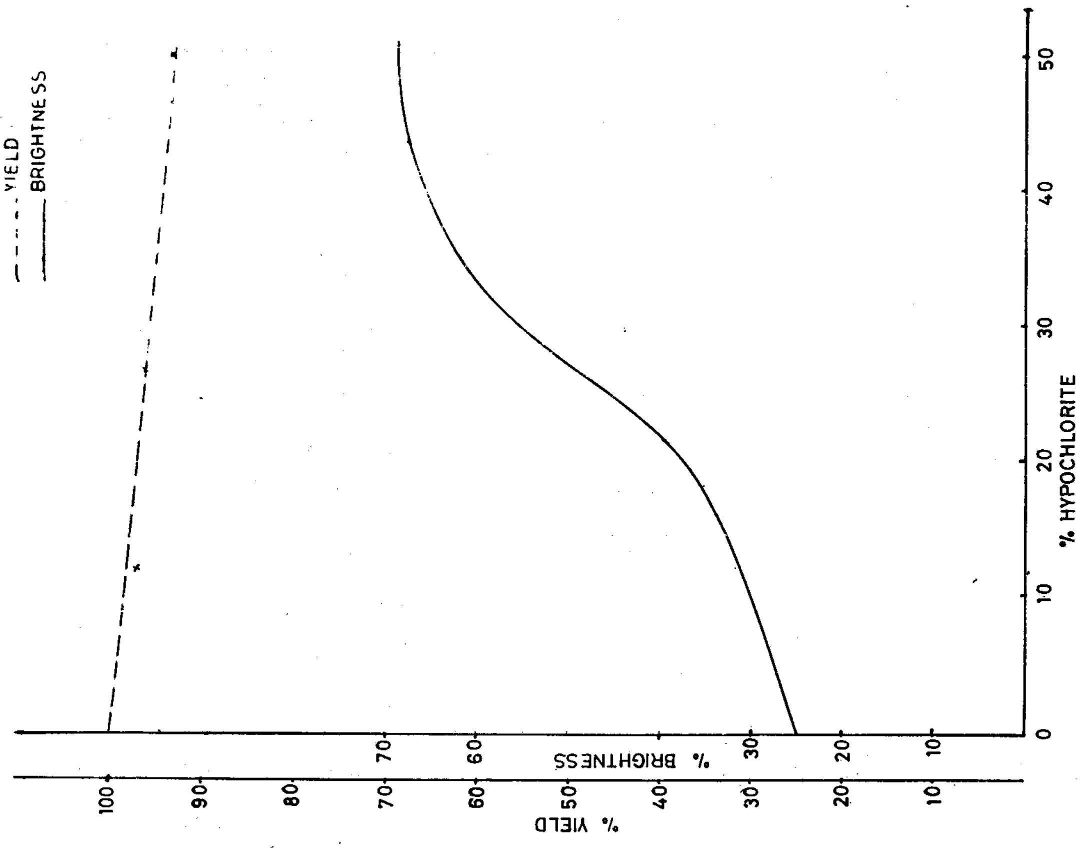

Fig.-1 HYPOCHLORITE BLEACHING EFFECT ON BRIGHTNESS AND YIELD

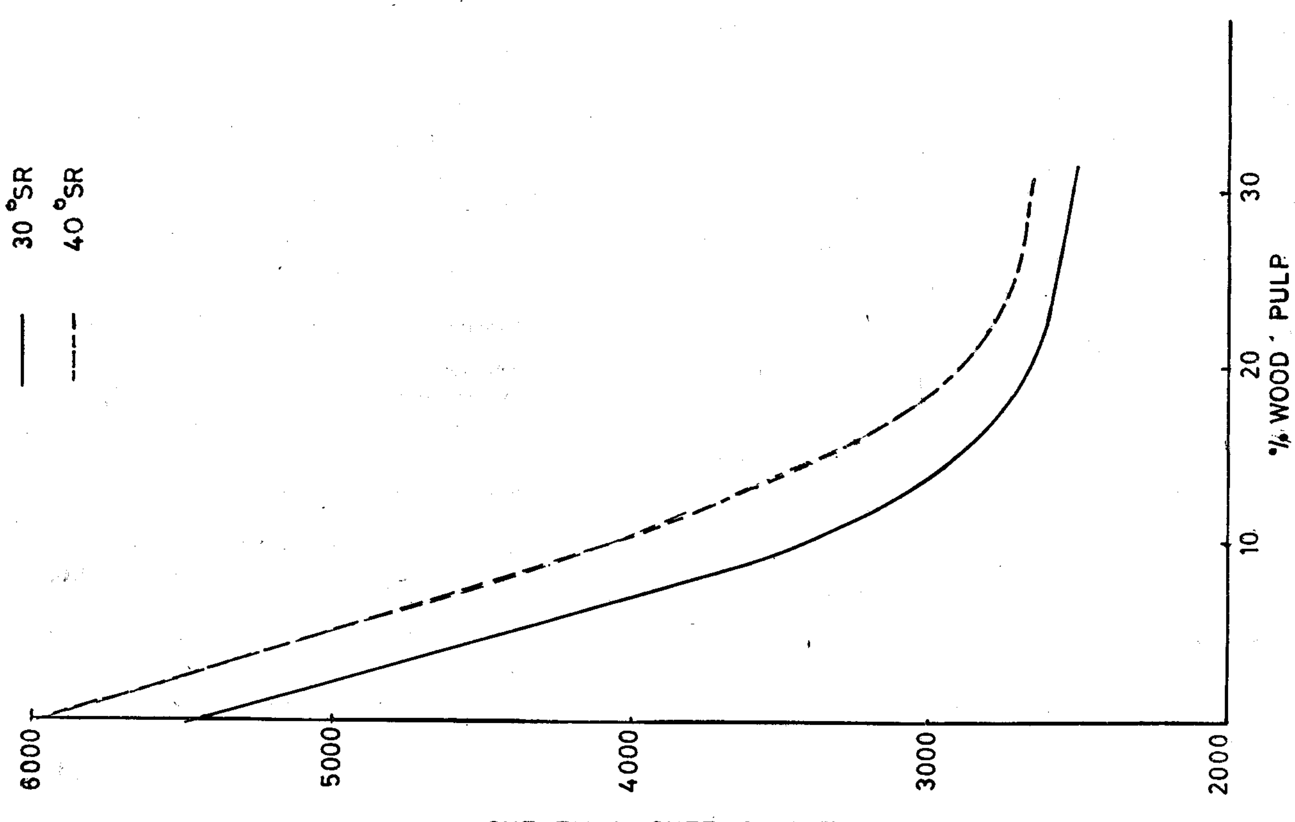

Fig. 2 EFFECT OF BLENDING COLD SODA WOOD PULP ON BREAKING LENGTH (Vide Table 4 A)

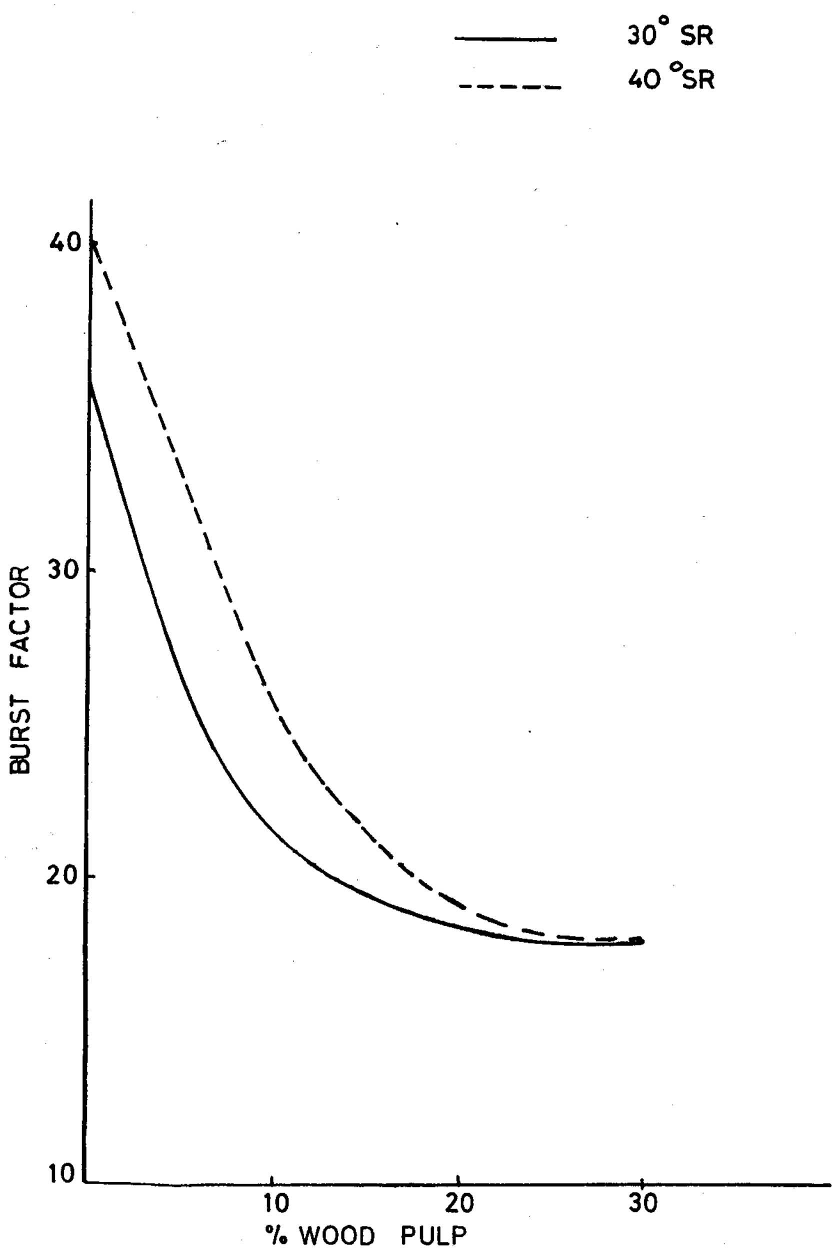

Fig. 3 EFFECT OF BLENDING WOOD PULP ON BURST FACTO(VIDE TABLE 4 A)

tion of the wood pulp is high and absorption is quick, hence does not make the chemical available to bamboo pulp in sufficient quantity. As a result the bamboo pulp also does not attain brightness and the whole pulp becomes dull.

Table 4 shows the effect of the blending of cold soda wood pulp with kraft bamboo pulp in unbleached and bleached condition. The strength properties are naturally decreased due to the less bonding nature of the semichemical pulp. The decrease in strength is abrupt when 10% of cold soda wood pulp is blended; afterwards it is gradual. The loss in strength properties of the papers with increased quantities of wood pulp is shown in figs. 2, 3 and 4. The results show that even though there is loss in the strength of paper, it is possible to blend the wood pulp upto 40% since some strength can be sacrificed for cheap grade of wrapping and printing papers. However, further improvement in strength may be obtained by variations in the pulp manufacturing process, chemical treatment and refining.

Combinations of bleaching in hypochlorite and peroxide stages are given in tables 5 and 6. These results show that the cold soda pulps of bamboo and wood can be bleached to appreciable brightness with hypo and peroxide or peroxide and hypo stages. Bamboo pulps have less bleachability than wood pulps. The C E H sequence in the first stage before peroxide has not given encouraging result in the case of bamboo pulp. The brightness values obtained in these combinations are quite satisfactory since the cold soda pulps will be blended with bleached kraft which is having higher brightness of about 80–82% and, the combined brightness can fall in the range of market acceptance. When hydrogen peroxide will be available in economical prices, this combination of bleaching sequence will be advantageous.

Table No. 7 shows the effect of blending of the peroxide bleached wood pulp with the alkali extracted bamboo pulp and then further bleached with calcium hypochlorite. These results indicate the practicability of using the peroxide treated semichemical pulps with bamboo pulp for further hypochlorite bleaching. Though there is some brightness drop, the same may be tolerated considering the higher yield of wood pulp and the consequent effect on the economics of the paper manufacturing. Using unbleached

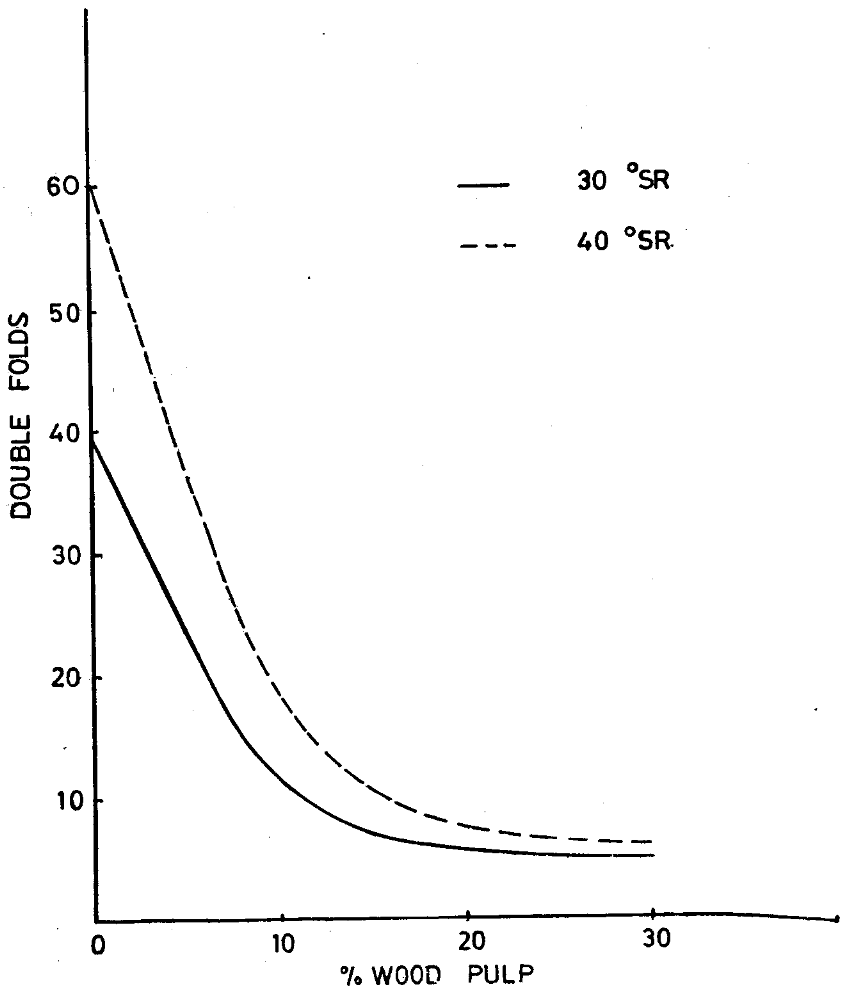

Fig. 4 EFFECT OF BLENDING WOOD PULP ON FOLDING ENDURANCE

soda pulp in the hypochlorite stage has definitely adverse effect on the brightness which has fallen from 78 to 67 or 74 to 64% respectively in the two experiments in spite of higher consumption of bleaching chemical. Table Nos. 8 and 9 give comparative results of bleaching with different oxidative and reductive bleaching agents. Conditions selected are such which are ideal as studied from literature to obtain best results and can be economical. These results show that within practical limits calcium hypochlorite is not a suitable chemical as the sole bleaching agent. However, its high oxidative effect is utilised in converting the chromophoric compounds in the cold soda wood pulps to such a stage that when further treated with hydrogen peroxide and sodium sulphite in subsequent stages they are decolourised substantially to attain final brightness of pulp to 61 per cent. Hydrogen peroxide is found to have high ability in improving the brightness of pulp if the bleaching is conducted in more than one stages. The quantity of the chemical required also will be reasonably less. As can be seen in table 7, this property can be utilised in giving 1 or 2-stage peroxide treatment to the cold soda pulp and then sending the pulp for further treatment with the hypochlorite. The results are found to be additive and the bleaching conditions can be so manoeuvred as to get the desired brightness. It can be seen that bleaching with peroxide and hypochlorite by changing either of the chemicals in the bleaching sequence gives additive results.

The effect of the reducing agents tried in our experiments is found not to be very much encouraging with the cold soda wood pulps. It may be because the colour compounds produced on reaction with the sodium hydroxide are more stable and are comparable with those produced by chemical pulping process. It is possible the reaction of sodium hydroxide is coupled with the high temperature caused during refining and more stable compounds are produced which require severe treatment of bleaching. The reducing agents are found to improve brightness levels only to 2.5–3.5 points when used as the sole bleaching agents. Hence these cannot be of practical value. However, when used in combination with hypochlorite and peroxide, they are found to raise the brightness to further higher levels. Sodium sulphite was able to improve brightness by 2–3 points whereas hydrosulphite and borohydride were able to raise the brightness by 8 points. This shows that when economics permit, use of hydrosulphite and borohydride will be advantageous in the final stage of bleaching.

Table No. 10 gives the effects of the different bleaching agents on the brightness stability of the pulps as shown by the post colour numbers. It can be seen that maximum colour reversion takes place with the hypochlorite bleached pulp. Next in order is the C E H sequence. Peroxide bleached pulps have more stability than the hypochlorite bleached

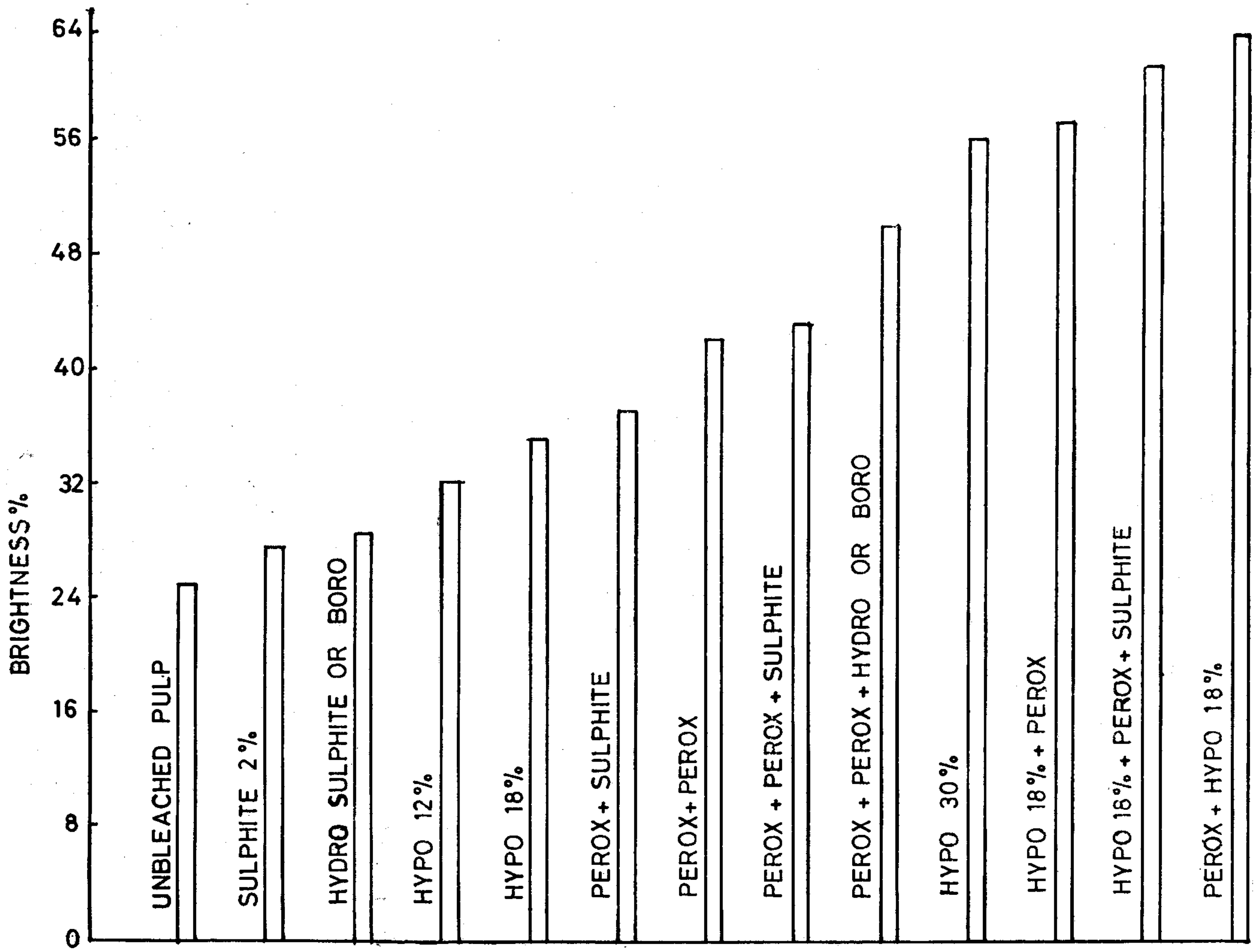

Fig. 5 EFFECT OF DIFFERENT BLEACHING SEQUENCES

ones. But when the reducing agents —sulphite, hydrosulphites and borohydrides—are used in the final stage after peroxide, brightness reversion is found to be minimum. This shows that in the lignin preservative bleaching of the cold caustic soda semichemical pulp it will be necessary to give a final treatment with one of the reducing agents to improve the stability of the pulp for colour reversion.

CONCLUSIONS:

Bleaching of the cold soda pulps of Andhra Pradesh hard woods tried was difficult due to the initial low brightness of the pulp which was about 25%. Normal methods of bleaching semichemical pulps gave brightness rise which is not sufficient to use the pulp for printing grades of paper. Hence, severe and combination bleaching methods are required. The following are our findings :

1 Straight hypochlorite bleaching does not raise the brightness to the required level until about 50% hypochlorite is used.

2 Multistage bleaching by C E H sequence using normal dosage of chlorine does not improve the brightness above 35% and 31% for wood and bamboo respectively. However, the yield losses are high.

3 Addition of cold soda pulps to the alkali extracted bamboo sulphate pulp and further bleaching with calcium hypochlorite reduces the brightness of the final pulp. Even after using 2.6% more of hypochlorite when 20% wood pulp was used, the brightness dropped from 77.5% to 69.0% (vide table 3B). Hence, using more than 20% wood pulp in mixed bleaching in the hypochlo-

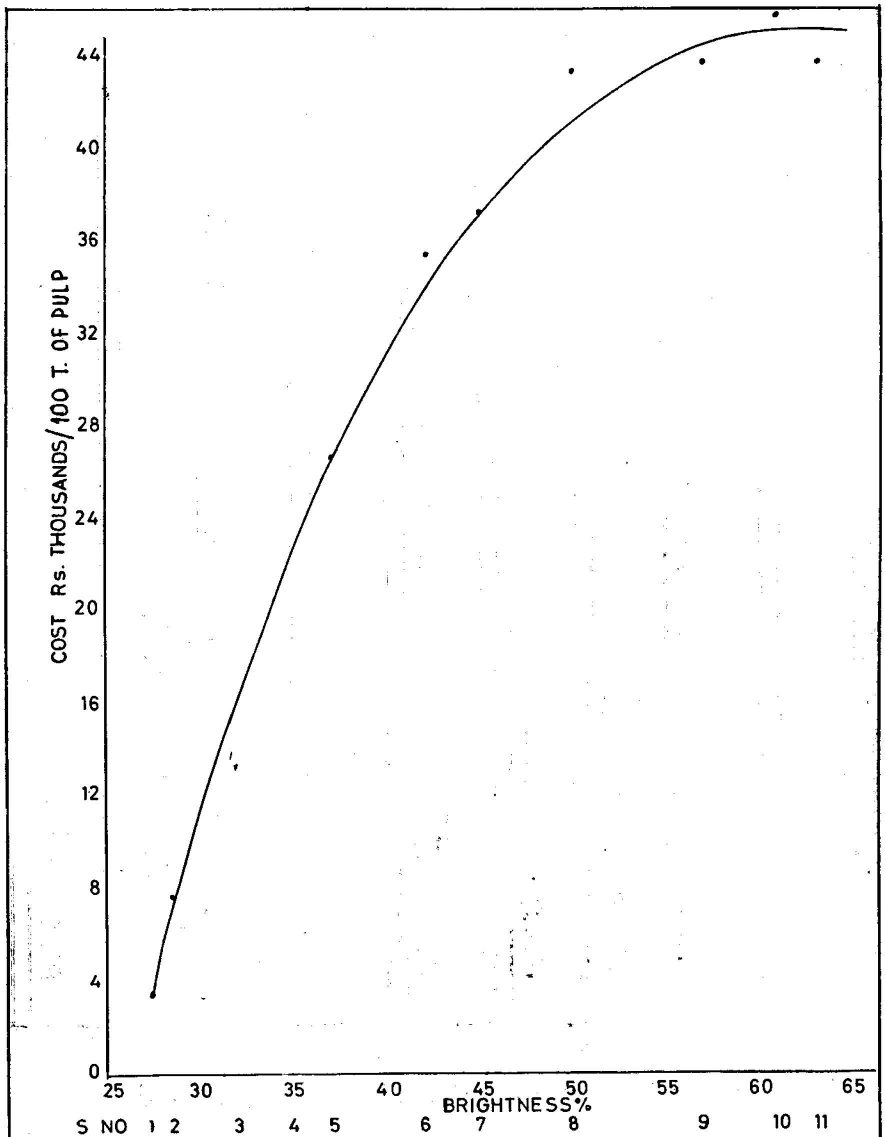

Fig.6 BLEACHING COST

rite stage will not be advisable.

4 Table No. 4A and 4B show that blending cold soda wood pulp with bamboo chemical pulp has adverse effect on the strength properties. Hence, this will also limit the possibility of using higher percentage wood pulp.

5 Peroxide bleaching can raise the brightness by about 22 points if the pulp is prebleached with hypochlorite.

6 Prebleaching wih peroxide before hypochlorite bleaching is advantageous; gives additive effect and can be practiced in the existing processing conditions in the plant at the A.P.P. Mills. However, 2–3% more hypochlorite will be required.

7 Reducing bleaching agents used individually are not beneficial as the brightness increase is low. They may, however, be used after combination of hypochlorite and peroxide bleaching to further raise the brightness by 2-8 points. Hydrosulphite and borohydrides are more effective than sodium sulphite. They also have beneficial effect on brightness stability.

The bleaching cost of the cold soda wood pulp with different bleaching agents and sequences is illustrated in fig. 6 and table No. II. It can be seen that the normal single stage bleaching by any of the chemicals does not raise the brightness to sufficeint level though the costs are high. The most workable sequences seem to be Peroxide+Hypo or hypo+peroxide. The costs appear to be high with the present prices of the peroxide bleaching chemicals, the same will be found to be very advantageous when the price of hydrogen peroxide and other chemicals will come down. Though the cost of bleaching may appear more the high pulp yield and advantages obtainable by the cold soda semichemical process, will more than compensate the higher cost of bleaching.

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