Studies on Colour Reversion of Bamboo Pulp Bleached with C-E-H Sequence

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SUMMARY

Bleached bamboo pulp has a tendency to discolour very fast. This ultimately reflects on the paper quality adversely. This paper deals with the contribution of some of the process variables during pulping and bleaching of bamboo sulphate pulps using CEH sequence towards colour reversion and also discusses the reaction mechanism of bleaching with hypochlorite and the role of oxycelluloses relating to colour reversion.

Unbleached pulp of high kappa number exhibits higher colour reversion on bleaching. The optimum chlorine charge required for chlorination is nearly one-fourth of the Kappa number. Both, over and underchlorination adversely affect the brightness stability besides lowering down the strength. Use of optimum alkali to get a final pH of 9.5-10.0 and higher temperature during alkali extraction improves the brightness stability. With the increase in Hypo consumption and temperature during hypostages the reversion increases besides pulp degradation. However, the retention time is reduced significantly at higher temperature to get the same level of brightness. An optimum pH of 8.5-9.0 is desirable for reducing colour reversion. At higher pH, though colour reversion is less but brightness level goes down in a given time because of slowing down of the reaction.

In case, the above contributory factors are taken into consideration, the colour reversion could be minimised.

INTRODUCTION

Bamboo is the major raw material for pulp and paper making in India and it shall continue to remain so in years to come. The advanced countries, in general, do not depend on bamboo. In comparison to all other raw materials used for pulp and paper making, bamboo pulp has been known to have a high degree of colour reversion tendency. The result has been that the quality of papers made from bamboo loose their original brightness in a very short time on storage, exposure to light or temperature, etc. which creates a major problem for the manufacturers as well as consumers.

Very little work has been donein the country or outside on this problem and to devise ways and means to minimise the same. The authors have taken up the study of this problem—a long and complex one—in stages. In the initial stage, the various processing parameters for alkaline sulfate pulping of bamboo Dendrocalamous strictus and chlorination, alkali extraction and hypochlorite

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treatment of resulting pulp, which all are easier to control and their effect on colour reversion in terms of post colour number and degradation (viscosity), etc. have been studied.

LITERATURE REVIEW

The brightness or the colour reversion is loss of brightness due to discolouration or yellowing that occurs during storage and/or exposure to heat or light, etc., Various efforts have been made to study the aspects related with colour reversion of pulp and paper in general.

The discolouration or brightness reversion is attributed to various constituents including ash and certain heavy metallic ions like ferric and cupperic[1]: Ions like Mg and Mn seem to improve the brightness stability[2]. The minor pulp constituents e.g., the resins (the extractives) also have pronounced effect on colour reversion[3]. The traces of lignin too contributes in this direction[4]. This lignin is not present in its original structure but in the form of low molecular weight fragments, some having quinoid structure and are coloured. Efforts have been made to relate to the colour reversion to the presence of lignin in the pulp, but its isolation with acid has not been sensitive enough. Although, initially the lignin constituents show an appreciable absorption at 280 m μ, with progressive fragmentation and hydrolysis, the absorption band disappears[5].

It has been reported that certain forms of oxycelluloses play an important role in colour reversion which depends very much on the extent to which the structure of carbohydrate molecules has been altered[6]. Low molecular carbohydrates like hemicelluloses, etc., also behave in similar manner but they are more sensitive and their effects is revealed by appreciable improvement in colour stability, once they are eliminated by cold caustic extraction ([5, 7, 8]).

The structure of cellulose molecules is chemically altered during the process of pulping, bleaching and paper making, prominently in the prior two processes. Oxidative degradation of cellulose chains may occur in presence of strong alkali at higher temperature during pulping and reducing type of oxycelluloses containing C=O and —CHO groups formed during bleaching with hypochlorite ([6, 9, 10, 11]).

EXPERIMENTAL

All the bleaching experiments, in general, were carried out using a CEH sequence. 50g OD pulp was taken in each case and disintegrated. The chlorination was carried out with chlorine water containing 4—5 gpl. available chlorine and the optimum chlorine was given at the rate of one fourth of the Kappa no. of the unbleached pulp as per the work carried out by Maheswari etal[14]. During alkali extraction, the desired pH was maintained by adding requisite quantity of alkali. At the hypo-stage, bleaching was carried out by calcium hypochlorite of 24-25 gpl. available chlorine. In both the stages, desired temperature was maintained with the help of constant temperature bath. After each stage, washing was carried out on the buchner funnel, using equal volume of fresh water. The filtrate in each case was tested for its pH and residual chlorine except in alkali extraction. Sheets from the finally bleached pulps were prepared for subsequent testing of viscosity and brightness. Constant conditions as given below were maintained throughout the experimentations related to bleaching, unless otherwise specified. The addition of various chemicals is calculated on OD Unbleached pulp basis.

		C	E	H
Consistency,	%	3.0	10.0	10.0
Temperature	°C	Ambient (29±2)	55	Ambient (29±2)
Reaction Time,	hr.	0.75	1.0	4.0

For Post Colour Number (P.C.No.), the sheets were kept for 1 hour at 95°C temperature and 95% Relative humidity in a colour reversion tester (Model No. KCL-JK,-154 by Finish Pulp & Paper Research Institute) and then taken out, air dried in a dark place and brightness measured.

P.C. No. was calculated (8) as follows :

$$\text{P.C. No.} = \left[\frac{(1-R\sigma=\infty_1)^2}{2R\sigma=\infty_2} - \frac{(1-R\sigma=\infty_1)^2}{2R\sigma=\infty_1} \right] \times 100$$

Where $R\sigma_1$ = Diffuse reflectance factor before aging.

$R\sigma_2$ = Diffuse reflectance factor after aging.

The study was carried out in stages and the characteristics choosen to evaluate the effect of various parameters were Brightness (Elrepho), Viscosity (CED) and P.C.No. In all the experiments, the raw material used was bamboo *Dendracalamous strictus* Except set no. 1, all bleaching experiments were carried out on unbleached pulps of Kappa No. 26±2 for a comparative study. The various tests were conducted as per TAPPI or ISI Standard procedure and the results are expressed on the basis of a minimum of three sets of experiments.

Set 1—EFFECT OF DELIGNIFICATION

2 kgs. O.D. bamboo chips were digested in a 15 lit. capacity, electrically heated digester. The cooking chemicals and 'H' factor were varied to get pulps of Kappa No. from 17-55. The coditions of cooking and results are recorded in Table-1.

The pulps of varying Kappa Nos. were bleached. At chlorination stage, optimum chlorine was given. Alkali at the extraction stage was so added to get a pH of 9.5-10.0. At hypo stage, a constant dose of hypo was given, except in one experiment where Kappa No. was very high (54.5), in order to get a uniform brightness of 79±1. The results are given in Table—2 and Fig—1.

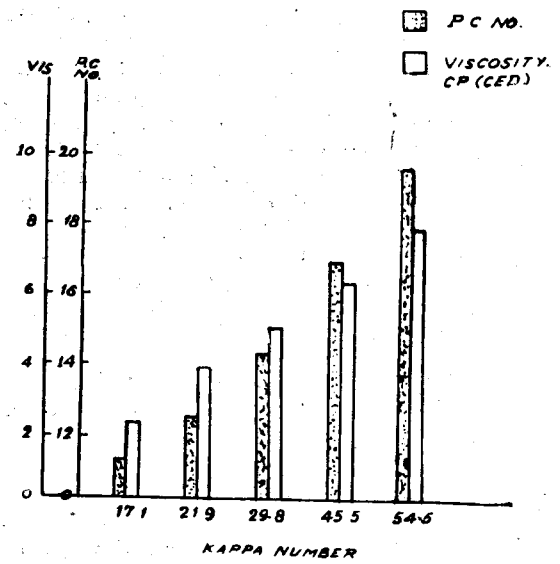

FIG 1. EFFECT OF DILIGNIFICATION OF BLEACHED PULP VISCOSITY AND PC.NO

Set 2—EFFECT OF OVER AND UNDERCHLORINATION

In this set, varying qualities of cholorine so adjusted as to give a range below and above the optimum chlorine requirement, were given at chlorination stage. In the alkali extraction, alkali was added to get a final pH around 9.5-10.0. Varying charge of hypochlorite was added in hypo stage to get a pulp brightness of 79±1. The results are given in Table—3.

Set 3—EFFECT OF ALKALI CHARGE IN ALKALI EXTRACTION

After the chlorination with the optimum chlorine, alkali was varied from 0 8 to 2.2% to obtain a final pH in varying degrees. At the hypo stage, hypochlorite addition was kept constant. Details are given in Table—4.

Set 4—EFFECT OF TEMPERATURE IN ALKALI EXTRACTION

In this set, optimum chlorine at chlorination stage and constant does of alkali and hypo in subsequent stages was given. The only change was that during alkali extraction, the temperature was varied from 40° to 70°C. The results are recorded Table—5.

Set 5—EFFECT OF HYPOCHLORITE CHARGE IN HYPO STAGE

Alkali extracted pulp of Kappa No. 7±1 obtained by optimum chlorination and alkali extraction was taken for hypo bleaching by varying the hypochlorite cnarge. The results are given in Table—6 and Fig. 2.

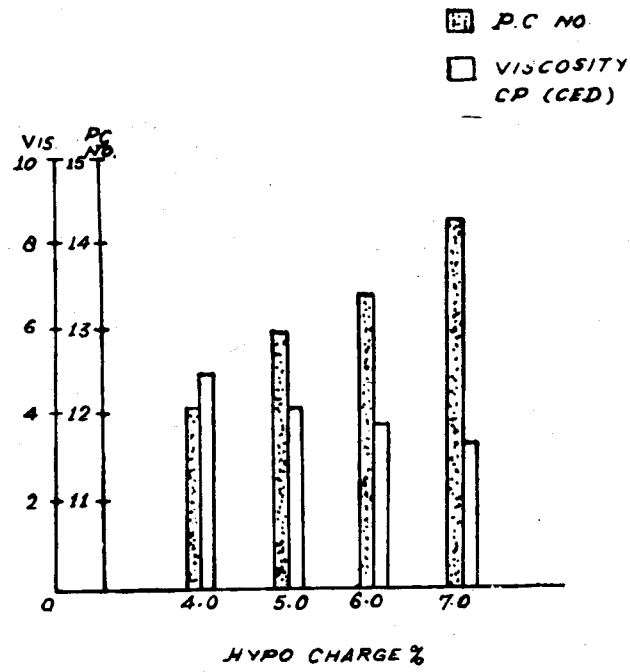

FIG. 2. EFFECT OF HYPO CHARGE ON VISCOSITY AND P.C. NO.

Set 6—EFFECT OF pH (BUFFER) IN HYPO STAGE

Experiments were carried out similar to set 5 with the exception that the pH of hypo bleaching was varied by adding varying doses of alkali. The results are given in Table—7.

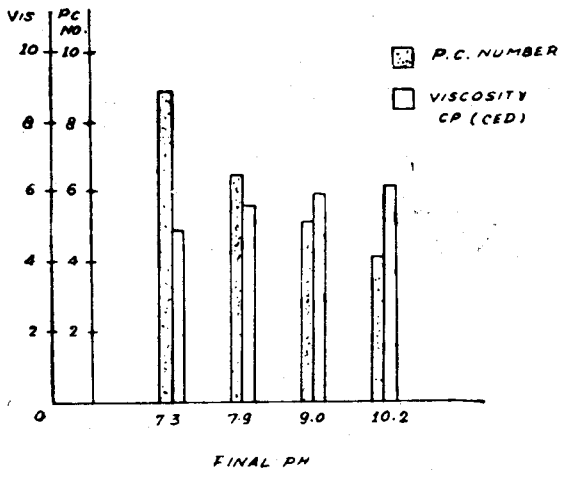

FIG. 3- EFFECT OF BUFFERING IN HYPO STAGE ON PULP VISCOSITY AND P.C.NUMBER.

Set 7—EFFECT OF TEMPERATURE IN HYPO STAGE

In this set, experiments were carried out similar to set 5 and 6 except varying the temperature and accordingly adjusting the retention time to get a brightness of 79±1. The results are recorded in Table-8.

OBSERVATIONS AND DISCUSSION

Unbleached pulp of varying Kappa Nos., when bleached with optimum dose of chlorine and alkali, required the same quantity of hypo to get a brightness of 79±1 except in case of very high Kappa No, (54.5) which could not attain this brightness level even after addition of extra hypo. The results (Table 2 and Fig. 1) indicate that with increasing Kappa No. of unbleached pulp, viscosity and colour reversion of the bleached pulp increases.

It is observed (Table-3) that with increase in chlorine as well as the alkali requirement during alkali extraction increases in order to obtain the desired pH level. On the contrary, total chlorine consumption is higher when over and under-chlorination is done. This is understandable since in the case of overchlorination some chlorine remains unused and is wasted. Similarly, in case of underchlorination, in subsequent hypostage, the chlorine requirement increases. The chlorine consumption is when optimum chlorine is added for chlorination. The viscosity of the finally bleached pulp increases with increase in charge of chlorine, only upto optimum level and then starts going down, on the contrary P.C. No. is minimum in case of optimum chlorine charge. The over and under-chlorination result in more colour reversion.

Results in Table-4 reveal that the P.C. No. of bleached pulp is lowest when final pH of alkali extraction is around 10. Below and over this, P.C. Nos. are higher.

Regarding the effect of temperature during alkali extration stage, results in Table-5 indicate that at lower temperature (say 40°C) the brightness

TABLE—1 PULPING DATA OF BAMBOO CHIPS

Particulars	Cook No 1.	Cook No 2.	Cook No. 3	Cook No. 4	Cook No. 5
Moisture in chips %	12.0	12.0	12.0	12.0	12.0
Active Alkali as Na20 on DO. Chips basis, %	22.0	20.0	17.0	15.0	13.0
Bath ratio	1:2.7	1:2.7	1:2.7	1:2.7	1:2.7
Cooking Schedule,					
50 to 170°c, hr	2.0	2.0	2.0	2.0	2.0
At 170°c, hr	1.5	1.5	1.5	1.0	1.5
H factor	1545	1545	1545	1085	1545
Pulp yield %,	40.6	42.1	41.9	42 6	42.7
Rejects, %	0 9	1.0	2.5	4.8	6.0
Kappa No.	17.1	21.9	29.8	45.5	54.5

N.B. 1) While liquor sulfidity—19.%
2) Water was used as diluent

TABLE—2 EFFECT OF DEGREE COOKING

Particulars	1	2	3	4	5
Kappa No.	17,1	21.9	29.8	45.5	54.5
Chlorination					
Cl_2 added, %	4.50	6.00	8.00	12.00	15.00
Cl_2 consumed %	3.95	4.95	7.12	10.80	14.58
final pH	2.0	1.9	1.7	1.5	1.4
ALKALI EXTRACTION					
NaOH added, %	1.2	1.4	1.8	2.6	3.2
final pH	9.5	10.0	9.60	9.80	10.5
Hypo Stage					
Cl_2 added	4.00	4.00	4.00	4.00	4.50
Cl_2 consumed %	3.60	3.44	3.49	3.46	4.20
final pH	6.8	6.7	6.7	6.7	6.1
Total cl_2 added, %	8.50	10.00	12.00	16.00	19.50
Total cl_2 consumed, %	7.55	8.39	10.61	14.26	18.78
Brightness, % (Elrepho)	78.2	79.3	78.0	80.5	73.4
Viscosity Cp (CED)	3.3	3.9	5.1	6.4	7.9
P.C. No.	11.2	12.5	14.3	16.9	19.7

TABLE—3 EFFECT OF OVER AND UNDER CHLORINATION

Particulars	1	2	3	4	5
CHLORINATION					
Cl_2, added	5.00	6 00	7.00	8 00	9.00
Cl_2, consumed, %	4.74	5.30	5.90	6.30	7.20
final pH	2.4	2.3	2.1	1.9	1.9
ALAKLI EXTRACTIO					
NaOH added, %	1.40	1.45	1.50	1.55	1.60
final pH	9.7	9.7	9.8	9.8	9.9
HYPO TAGE					
Cl_2 added, %	7.50	6.00	5.00	5.00	4.50
Cl_2 consumed, %	7.01	5.57	4,57	4.66	4.17
final pH	6.0	6.6	6.9	6.9	6.8
Total cl_2 added, %	12.50	12,00	12.00	13.00	13.50
Total cl_2 consumed, %	11.75	10.87	10.47	10.96	11.37
brightness, (Elrepho), %	80.3	81.0	79.7	79.9	79.3
Viscosity cp (CED)	3.1	3.5	4.9	4.2	4.1
P.C. No.	17.6	15.0	14.8	15.2	19.8

N.B.—Nnbleached pulp kappa no. 26.4

TABLE—4 EFFECT OF ALKALI CHARGE IN ALKALI EXTRACTION

Particulars	1	2	3	4	5
CHLORINATION					
Cl_2 added, %	6.50	6.50	6.50	6.50	6.50
Cl_2 consumed, %	5.55	5.40	5.49	5.42	5.45
Final pH	1.8	1.8	1.8	1.8	1.8
EXTRACTION					
NaOH added, %	0.8	1.1	1.2	1.7	2.2
Final pH	6.8	7.7	8.9	10.1	11.3
HYPO STAGE					
Cl_2 added. %	4.50	4.50	4.50	4.50	4.50
Cl_2 consumed, %	4.10	4.02	4.03	4.02	4.02
final pH	7.0	7.0	7.2	7.2	7.3
Total cl_2 added, %	11.00	11.00	11.00	11.00	11.00
Total cl_2 consumed %	9.65	9.42	9.52	9.44	9.47
Brightness (Elrepho) %	77.6	78.7	78.9	78.8	79.1
Viscosity cp. (CED)	5.3	4.8	5.2	5.1	5.0
P.C. No.	16.4	15.5	13.3	12.6	13.6

N.B. Unbleached Kappa No.—26.4

TABLE—5 EFFECT OF TEMPERATURE IN ALKALI EXTRACTION

Particulars		1	2	3	4
CHLORINATION					
Cl_2 added	%	6.50	6.50	6.50	6.50
Cl_2 consumed	%	5.17	5.10	5.14	5.20
Final pH		2.1	2.0	2.0	2.0
EXTRACTION					
NaOH added	%	1.7	1.7	1.7	1.7
Temperature	°C	40	50	60	70
Final pH		10.2	10.1	9.7	9.8
HYPO STAGE					
Cl_2 added	%	4.50	4.50	4.50	4.50
Cl_2 consumed	%	4.05	4 06	4.01	3.96
Final pH		7.2	7.3	7.3	7.3
Total Cl_2 added	%	11.00	11.00	11.00	11.00
Total Cl_2 consumed	%	9.22	9.16	9.15	9.16
Brightness (Flrepho)	%	78.2	79.8	79.8	79.7
Viscosity, cp (CED)		4.6	4.8	4.4	4.3
P.C. No.		16.4	14.9	14.2	12.4

N.B.—Unbleached Pulp Kappa No. 254

TABLE—6 EFFECT OF HYPO CHARGE IN HYPO STGE

Particulars		1	2	3	4
HYPO STAGE					
Cl_2 added	%	4.30	5.00	6.00	7.00
Cl_2 consumed	%	3.43	4.42	5.34	6.34
Final		6.9	6.8	6.7	6.5
Brightness (Elrepho)	%	80.6	82 0	83.4	83.4
Viscosity, cp (CED)		5 0	4.2	3.8	3.4
P.C. No.		12.1	13.0	13.4	14 3

TABLE—7 EFFECT OF pH (BUFFER) IN HYPO STAGE

Particulars		1	2	3	4
HYPO SSAGE					
Cl_2 added	%	4.00	4.30	4.00	4.00
Cl_2 consumed	%	3.70	3.43	3.27	3.23
Buffer(NaOH)added	%	0.25	0.8	1.2	1.5
Retention Time	Hr.	4.0	4.0	5.0	5.0
Final pH		7.3	7.9	9.0	10.2
Brightness	%	78.6	78.6	78.0	73.2
Viscosity cp (CED)		4.9	5.6	6.0	6.2
P.C.No.		8.6	5.6	5.2	4.2

TABLE—8 EFFECT OF TEMPERATURE IN HYPO STAGE

Particulars		1	2	3	4
HYPG STAGE					
Cl_2 added	%	4.50	4.50	4.50	4.50
Cl_2 consumed	%	4.25	4.30	4.26	4.30
Temperature	°C	30	40	50	60
Retention Time	hr.	4 00	2.30	0.50	0.50
Final pH		6.7	6.5	6.8	6.4
Brightness (Elrepho)	%	81.0	81.0	79.3	80.2
Viscosity cp (CED)		3.9	3.7	3.8	3.6
P.C. No.		8.8	9.1	9.4	9.8

obtained is slightly lower when compared to higher temperatures, which further have practically no effect on brightness. The colour reversion decreases with the increase in temperature. As regards viscosity, initially it increases and then starts dropping down. Hence, a compromise shall have to be made.

With increasing hypo charge, pulp brightness initially increases, but then gets stabilised. The viscosity decreases and P.C. No. increases with increasing charge of hypo (Table-6 and Fig. 2)

An important observation, when the pH at the hypostage is increased (Table 7 and Fig. 3), is that P.C. No. shows a signifinicant reduction whereas viscosity increases. However, at higher pH it is difficult to attain the desired brightness under the given conditions of bleaching. A pH arcund 8.0-8.5 could be considered to be a compromising figure.

Table 7 reveals that increase in temperature at hypo stage, hypo charge remaining constant, the retention time is to be reduced to obtain the same level of brightness. The effect on viscosity is though insignificant, but there is a decreasing trend with increase in temperatures even after reducing retention time. The P.C. Nos. show an increasing trend with increase of temperature.

CONCLUSION

The colour reversion of bleached bamboo pulps, being a complex phenomenon, as a result of several factors, many unknown, can be minimised to an appreciable extent by controlling the variables during the process of pulping and bleaching, in existing working conditions of the Indian Pulp and Paper industry.

With the increase in Kappa No. of unbleached pulp, the viscosity of bleached pulp increases on one hand and the colour reversion on the other. Hence, where a paper is to be made, with stability of brightness being an important characteristic, an optimum Kappa Number i.e. neither too high nor too low is desired, subject to the prevailing conditions in a mill.

During chlorination, the optimum chlorine at a rate of one-fourth of the Kappa number of unbleached pulp, reduces colour reversion tendency appreciably. Under and overchlorination, both have an adverse effect in this regard. During alkali extraction again, optimum alkali to give a final pH of 9.5-10.0 at an elevated temperature helps in bringing down the colour reversion tendency. However, as too high a temperature leads to pulp degradation, an optimum temperature say 50°-60°C could be considered adequate. Lower temperature results in more colour reversion.

The more the charge of hypo used for hypo bleaching, more the degradation of pulp and colour reversion. The minimum dose of hypo to obtain maximum possible brightness (as after a particular limit increase in hypo does not increase brightness) would be advantageous without sacrifying the brightness provided the chlorination and alkali extraction are carried out with optimum charge of chemicals. The higher the pH at this stage, the better its brightness stability and viscosity. However, at higher pH, the rate of bleaching reduces and hence a pH around 8·5 could be considered to be reasonable in terms of colour reversion, strength and brightness. With regards to the temperature of hypo bleaching, the viscosity reduces and colour reversion tendency increases, and hence lower temperature would be helpful in this respect. In case, a higher temperature is unavoidable in view of inadequate capacity of hypostage, the retention time has to be correspondingly reduced in order to have no adverse effect.

The various findings of this study show that it is possible to control the problem of colour reversion in bleached bamboo pulps *D. strictus* to an appreciable extent by following a CEH (H) sequenee of bleachings, which is commonly used in most of Indian Pulps and Paper mills, if the variables described above are controlled.

In order to study this problem critically and reduce colour to a minimum acceptable range, it may be necessary to study and incorporate radical changes including a multiple bleaching sequence, using chlorindioxide, peroxide, etc., which are commonly practicized in other countries. However, the present study was confined to what can be done in the existing prevailing conditions.

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