Reduction in Pollution Load by Alkali/Oxygen Delignification of Paper Grade Mill Pulp under C-Ep-H-D and CD-Ep-H-D Bleaching Sequences.

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With the objective of reduction in pollution load generated from conventionally produced paper grade pulp from Bamboo & Hard Wood (Kappa No 24.4) was alkali/oxygen delignified followed by C-Ep-H-D & CD-Ep-H-D bleaching sequences to achieve 87± 1% P.V. pulp brightness. It was observed that alkali/oxygen delignified mill pulp bleached under C-Ep-H-D sequence requires lower chlorine demand under O-C-Ep-H-D and O-CD-Ep-H-D sequences which resulted in improved bleached pulp quality, reduction in pulp shrinkage and pollution load (COD, dissolved solids and chloride) compared to conventional C-Ep-H-D bleaching sequence.

INTRODUCTION

Strict legislation of central pollution control board in the country and increasing cost of energy, chemicals, utilities and increasing demand of high brightness paper has forced the Indian paper industry to give serious thought for the modification of present bleaching practices. Therefore incorporation of pre stage oxygen delignification and reduction of chlorine & its compounds during bleaching is being felt. The use of oxygen delignification system has steadily increased worldwide since first commercial installation in 1970[1]. With roughly 40% of North American bleach plants use oxygen delignification systems. Almost 100% of bleach plants in Scandinavia use oxygen delignification[2-4]. Though oxygen pre bleaching and chlorine dioxide substitution in bleaching of pulps are well established processes in developed countries for their raw material pulps but little information is available on Indian fibrous raw materials accordingly there is need for in depth laboratory studies before suitably adopting these technologies for the commercial exploitation.

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Oxygen delignification is used to reduce 35-50% of original lignin content of the pulp & is run under medium consistency (8%-12%) conditions.

Oxygen delignification studies by many researchers[5-14] highlights the multiple advantages of oxygen delignification. Significant reductions are obtained in pollution load[15] (COD, BOD & AOX), power[16] and wastewater generation[17]. Tangible benefits include savings through reduced chemicals for pulping and bleaching[18], higher pulp yield and waste water treatment costs. Other significant benefits can be realized through partial closure of fibre line by recycle of oxygen pre bleach stage effluent to chemical recovery system.

Oxygen delignification system do not typically supply the higher rates of return on capital employed demanded by the industry today[19]. But the environmental benefits and lower operating cost of oxygen delignification as compared to alternate bleaching sequences are well acknowledged throughout the industry. Like chlorine, oxygen undergoes one electron transfer oxidation process but also reduced to hydrogen peroxide that selectively oxidizes the chromophoric structures. In a sense oxygen bleaching initiates reaction characteristics for both acid chlorination and peroxide bleaching. As a result substantial lignin removal as well as improvement in brightness is obtained[20]. The main modifications observed on residual lignin during oxygen delignification are increase in carboxyl groups and decrease in free phenolic groups[21-23].

The trend today is to implement two stage oxygen delignification[24,25].

EXPERIMENTAL DETAILS

Mill pulp (Kappa No 24.5) comprising of 55% mixed varieties of bamboo and 45% mixed hard woods was alkali/oxygen delignified (using 2.5% alkali, 0.5% Magnesium Sulphate, oxygen pressure 5.0 Kg/cm^2, reaction temperature 105°C and retention time 60 minutes) in an autoclave. There was gain of 8.0 degrees brightness in mill pulp (Table.1).

The delignified pulp was evaluated for pulp kappa, pulp shrinkage%, end pH and gain in pulp brightness (Table. 1). The effluent generated was also evaluated for various physico-chemical properties.

Fibre classification of mill pulp (unbleached and alkali/oxygen treated pulps) was carried out in a Bauer Mcnett classifier and the results are reported in Table.2.

Mill pulp (unbleached and alkali/ oxygen treated) were beaten to 30° SR freeness and evaluated for physical strength properties as per Tappi standards. (Table.3.).

Mill pulp was also bleached under C-Ep-H-D sequence and alkali/ oxygen pre-treated mill pulp was bleached under C-Ep-H-D and CD-Ep-H-D sequences and the results are reported in Table.4.

Pollution load in terms of COD, suspended solids, dissolved solids and chloride content generated under these bleaching sequences is tabulated in Table.5. Fibre classification & evaluation of physical strength properties of mill pulp bleached under various bleaching sequences are given in Table.6 & Table.7 respectively.

Table 1 : Alkali / Oxygen delignification of mill pulp

Particulars	Mill pulp
Kappa No. of pulp	24.4
Initial pulp brightness, % PV	22.0
Alkali Added, %	2.5
$MgSO_4$ added, %	0.5
Final pulp brightness, %PV	30.0
Pulp Shrinkage, %	3.5
Pulp Kappa of Alkali / Oxygen delignified pulp,	14.6
Pulp Kappa reduction, %	40.16
Effluent analysis	
pH	10.4
COD, mg/l	3838
Chloride, mg/l	100
S. Solids, mg/l	46
D. Solids, mg/l	5816
Total Solids, mg/l	5862
Colour, Pt-Co unit	7500

Table 2 : Fiber Classification of mill unbleached pulp and Alkali/ Oxygen delignified pulp.

Mesh Size	Mill unbleached pulp	Mill Alkali/Oxygen delignified pulp.
	Retention %	
+ 40	47.5	45.4
- 40 + 70	13.0	15.5
- 70 + 100	11.1	8.5
- 100 + 140	3.2	4.7
- 140	25.2	25.9
Total	100.00	100.00

Table 3 : Physical strength properties of mill unbleached pulp and Alkali/ Oxygen delignified pulp.

Particulars	Mill unbleached pulp	Mill Alkali/ Oxygen delignified pulp.
Final Freeness °SR of pulp.	30	30
Beating revolution in P.F.I. mill rpm.	5000	5000
Bulk c.c / gram	1.54	1.52
Tensile Index, Nm. / g	60.96	59.08
Burst Index, K Pa. m^2/ g	4.06	4.08
Tear Index, m Nm^2/ g	6.59	6.48
Double fold,	246	235

RESULTS AND DISCUSSIONS

Pulp shrinkage in alkali/oxygen delignification stage was observe to be 3.5% that reduced pulp Kappa by 40.2%. The complete elimination of cellulose degradation during oxygen bleaching thus seems impossible, however, undesirable degradation of cellulose during oxygen bleaching could be significantly diminished by the presence of $MgCO_3$[26]. Higher amount of COD, suspended solids, dissolved solids and colour in the effluent was observed to be generated from mill pulp. The spent liquor from alkali/oxygen delignification stage can be recycled mixed with black liquor, evaporated and burnt in chemical recovery, thereby reducing the pollution load considerably.

Fibre classification results of mill pulp with and without alkali/ oxygen delignification tabulated in Table.2 show that fibre retention percentage on 40 mesh was lower compared to mill unbleached pulp.

Table 4 : Bleaching of mill unbleached pulp under C- Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D sequences.

Particular	Mill pulp bleached under Sequence.		
	C- Ep-H-D (Kappa No.24.4)	O-C-Ep-H-D (Kappa No.14.6)	O-CD-Ep-H-D (Kappa No.14.6)
Chlorination Satge.			
i) Chlorine applied, %	5.0	3.0	2.7
ii) Chlorine dioxide applied, % (as available chlorine)	-	-	-
iii) Chlorine cosumed, %	4.94	2.97	2.67
iv) End pH	1.9	2.2	2.2
v) Consistency	Room	Room	Room
vi) Temp. °C	60	60	60
Alkali Extraction Stage.			
i) Caustic applied, %	2.0	1.0	1.0
ii) H_2O_2 applied, %	0.4	0.4	0.4
iii) End pH,	10.0	9.8	10.2
iv) Consistency, %	10.0	10.0	10.0
v) Temp. °C	65± 1	65± 1	65± 1
vi) Time, mnts	60	60	60
Calcium Hypo chlorite Stage.			
i) Hypo chlorite applied, %	3.0	2.0	2.0
ii) Hypo chlorite consumed, %	2.78	1.8	1.36
iii) Sulphamic Acid, %	0.1	0.1	0.1
iv) Buffer added, %	1.1	0.5	0.5
v) End pH	8.7	8.0	8.8
vi) Consistency, %	10.0	10.0	10.0
vii) Temp. °C	40± 1	40± 1	40± 1
viii) Time, mnts	120	120	120
Chlorine dioxide Stage.			
i) Chlorine dioxide applied, %	0.6	0.6	0.6
ii) Chlorine dioxide consumed, %	0.5	0.52	0.53
iii) End pH,	6.8	5.2	6.0
iv) Consistency, %	10.0	10.0	10.0
v) Temp. °C	70± 1	70± 1	70± 1
vi) Time, mnts	120	120	120
Final Results.			
i) Total chlorine applied, %	8.0	5.0	4.7
ii) Total chlorine consumed, %	7.72	4.77	4.03
iii) Pulp Brightness, % P.V	87.0	87.0	88.0
iv) Bleached pulp shrinkage, % (on O.D. pulp)	12.0	10.1	10.5
v) Pulp Viscosity (0.5% C.E.D), Cps	7.5	8.2	8.5

Table 5 : Effluent analysis of mill pulp bleached under C-Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D sequences.

Particular	Mill pulp C-Ep-H-D Sequence				Mill pulp O-C-Ep-H-D Sequence				Mill pulp O-CD-Ep-H-D Sequence			
	Chlorination stage	Alkali Extraction stage	Hypo Chlorite stage	ClO_2 stage	Chlorination stage	Alkali Extraction stage	Hypo Chlorite stage	ClO_2 stage	Chlorination stage	Alkali Extraction stage	Hypo Chlorite stage	ClO_2 stage
pH	1.9	10.0	8.7	6	2.2	9.8	8.0	5.1	2.2	10.2	8.8	6.0
C.O.D. mg/L	576	2495	1137	230	355	967	932	263	393	1236	620	211
S. Solids Mg/L	136	330	416	360	182	154	458	134	168	162	374	100
D. Solids Mg/L	6078	5074	10948	1808	3352	2232	7872	1860	3542	2696	6996	1780
Total Solids Mg/L	6214	5404	11364	2168	3534	2386	8330	1994	3710	2858	7370	1880
Chloride Mg/L	3500	900	5000	300	2200	400	3400	300	1600	250	3260	270

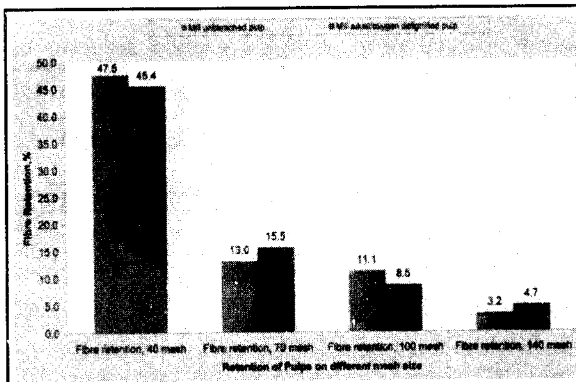

Fig. 1 : Fibre Classification of mill unbleached pulp and alkali/oxygen delignification pulps

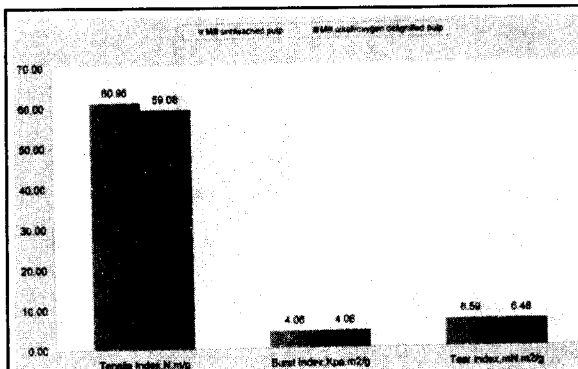

Fig. 2 : Physical Strength properties of unbleached mill pulp and alkali/oxygen delignification pulps

Retention of mill pulp (with and without alkali / oxygen delignification) on different mesh is projected in Fig.1. Physical strength properties of mill pulp (with and with out alkali delignification) are reported in Table.3 Physical strength properties of alkali/oxygen delignified pulps were observed to be slightly on lower side compared to non alkali/ oxygen delignified pulps as is evident from Fig-2.

Bleaching of Mill Pulp Under C-Ep-H-D., O-C-Ep-H-D And O-CD-Ep-H-D Sequences:

Mill pulp (Kappa No.24.4) and its alkali/oxygen delignified pulp (Kappa No 14.6) were bleached under C-Ep-H-D bleaching sequence to achieve 87 ± 1% P.V. pulp brightness. Alkali / oxygen delignified mill pulp was also bleached under CD-Ep-H-D bleaching sequence to get improved quality of bleached pulp (Table.4).

It was observed that pulp shrinkage was more in C-Ep-H-D bleaching sequence compared to O-C-Ep-H-D and O-CD-Ep-H-D sequences as a result of lower amount of available chlorine consumed in chlorination and hypochlorite stages.

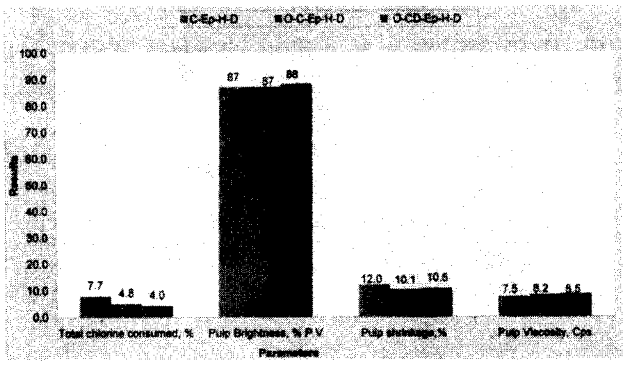

Fig. 3 : Bleaching of mill pulp under C-Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D sequences

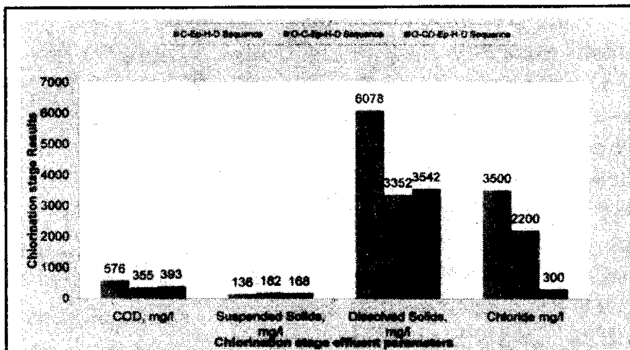

Fig. 4 : Chlorination stage effluent analysis of mill pulp bleached under C-Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D sequences

Table 6 : Fibre Classification of mill pulp bleached under C-Ep-H-D, O-C-Ep-HD and O-CD-Ep-H-D sequences.

Mesh Size	Mill pulp C-Ep-H-D bleached pulp	Mill pulp O-C-Ep-H-D bleached pulp	Mill pulp O-CD-Ep-H-D bleached pulp
	Retention %		
+ 40	47.5	49.1	49.3
- 40 + 70	14.8	15.8	17.1
- 70 + 100	12.2	13.4	12.6
- 100 + 140	4.0	3.3	4.7
- 140	21.5	18.4	16.3
Total	100.00	100.00	100.00

In chlorination stage substitution, addition as well as oxidation reaction take place to form chlorolignins. Nearly one half of the lignin is lost from pulp during chlorination stage and rest of the degraded lignin goes into the liquor during caustic extraction stage[27]. Introduction of chlorine dioxide in chlorination stage improved final bleached pulp viscosity but pulp shrinkage was on higher side.

Total chlorine consumption was reduced more than 40% in O-C-Ep-H-D and O-C-D-Ep-H-D bleaching compared to blank sequences experiment. Total chlorine consumption, pulp brightness, pulp shrinkage% and viscosity of bleached pulps under different sequences are highlighted in Fig.3.

Effluent characteristics of mill pulp bleached under C-Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D bleaching sequences

Effluent parameters examined at each stage of bleaching of mill pulp under C-Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D sequences are reported in Table.5.

In chlorination stage of O-C-Ep-H-D sequence COD, dissolved solids and chloride reduction was 38.4%,44.8% and 37.1% whereas in CD stage of O-CD-Ep-H-D sequence it was 31.8%, 41.7% and 54.3% respectively compared to C-Ep-H-D sequence. Effluent parameters in chlorination stage of various bleaching sequences are highlighted in Fig.4.

Effluent parameters viz COD, suspended solids, dissolved solids and chloride were reduced in

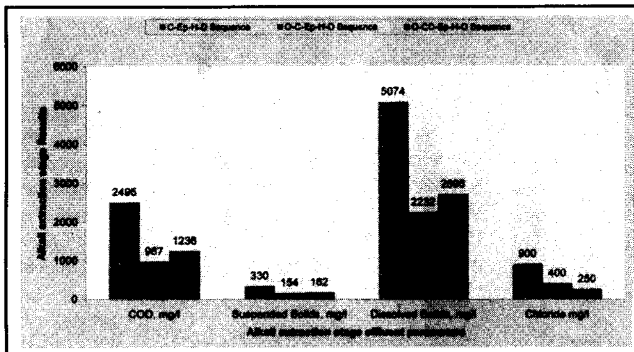

Fig. 5 : Alkali extration stage effluent analysis of mill pulp bleached under C-Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D sequences

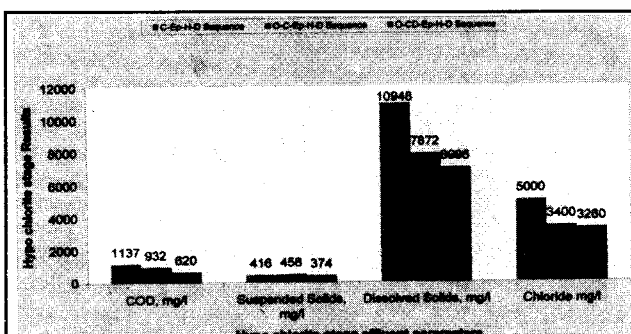

Fig. 6 : Hypo chlorite stage effluent analysis of mill pulp bleached under C-Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D sequences

caustic extraction stage of O-CD-Ep-H-D sequence by 61.2%, 53.3%, 56.0% and 55.5% respectively whereas in O-CD-Ep-H-D sequence these were reduced 50.5%, 50.9%, 46.9% and 72.2% respectively compared to caustic extraction stage of C-Ep-H-D bleaching sequence. COD, suspended solids, dissolved solids, and chloride in caustic extraction stage effluent were considerably reduced compared C-Ep-H-D bleaching sequence (Fig.5).

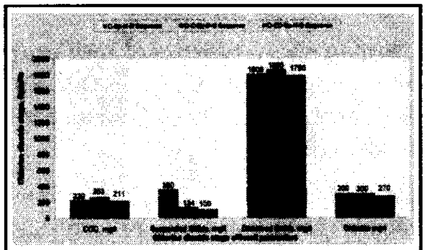

Fig. 7 : Chlorine dioxide stage, effluent analysis of mill pulp bleached under C-Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D Sequences

In calcium hypochlorite stage of O-C-Ep-H-D bleaching sequence COD, suspended solids, dissolved solids, and chloride, reduction was 18.0%, Nil, 28.1 % and 32.0% whereas in O-CD-Ep-H-D sequence it was 45.5%, 10.1 %, 36.1 % and 34.8% respectively compared to hypochlorite stage effluent of C-Ep-H-D bleaching sequence. COD, suspended solids, dissolved solids and chloride in hypochlorite stage

Table 7 : Physical strength properties of mill pulp bleached under C-Ep-HD, O-C-Ep-H-D and O-CD-Ep-H-D sequences.

Particulars	**Mill pulp** C-Ep-H-D sequence bleached pulp	O-C-Ep-H-D sequence bleached pulp	O-CD-Ep-H-D sequence bleached pulp
Beating revolution in P.F.I. mill rpm,	4250	5200	5400
Final Freeness, °SR of beaten pulp,	30	30	30
Bulk, c.c. /gram	1.42	1.41	1.41
Tensile Index, Nm. / g.	47.89	55.39	57.47
Burst Index, K Pa. m^2 /g	3.49	4.01	4.05
Tear Index, m Nm^2 /g	5.14	6.87	7.09
Double fold	151	219	297

effluent of C-Ep-H-D sequence were on higher side compared to other two bleaching sequences as depicted in Fig.6

In chlorine dioxide stage effluent of O-C-Ep-H-D and O-CD-Ep-H-D sequences higher reduction in suspended solids percentage was observed against chlorine dioxide stage of C-Ep-H-D bleaching sequence. Various parameters of ClO_2 stage effluent of C-Ep-H-D sequence are compared with O-C-Ep-H-D and O-CD-Ep-H-D sequences in Fig.7.

Evaluation of mill pulp bleached under C-Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D sequences

Fibre classification results of mill pulp bleached under C-Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D bleaching sequences reported in Table.6 shows that reduction in chlorine and hypo chlorite consumption helped in increasing the fibre retention percentage on 40 & 70 mesh whereas fines percentage was reduced in O-C-Ep-H-D and O-CD-Ep-H-D bleaching sequences. Comparison of fibre retention on different mesh under different bleaching sequences is highlighted in Fig.8.

Mill pulp bleached under C-Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D sequences evaluated for strength properties (Table.7) show that the pulp bleached under O-C-Ep-H-D

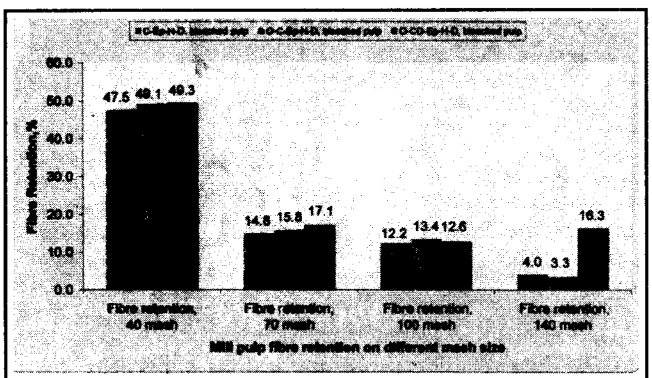

Fig. 8 : Fibre Classification of mill pulp bleached under C-Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D sequences

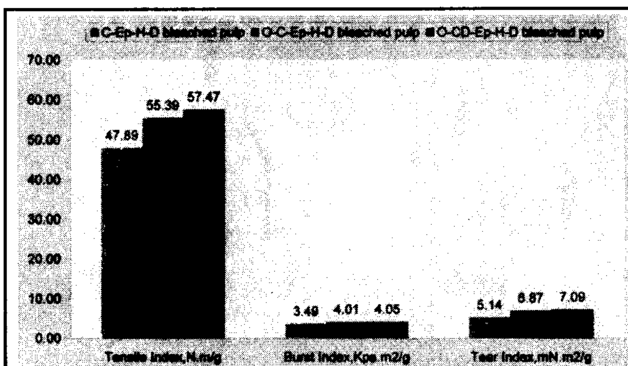

Fig. 9 : Physical Strength properties of mill pulp, bleached under C-Ep-H-D, O-C-Ep-H-D and O-CD-Ep-H-D sequences

and O-CD-Ep-H-D sequence require higher beating revolution to achieve the desired pulp freeness and has higher physical strength properties than C-Ep-H-D sequence bleached pulp. Tensile Index, Burst Index and Tear Index of mill pulp bleached under different bleaching sequences is projected in Fig.9.

CONCLUSION

Alkali/oxygen delignification of mill pulp (Kappa. 24.0) resulted in reduction of pulp Kappa by 40%. Alkali/oxygen delignified mill pulp bleached under C-Ep-H-D and CD-Ep-H-D bleaching sequences resulted in lower pulp shrinkage, lower pollution load at each stage of bleaching and higher physical strength properties than mill pulp bleached under C-Ep-H-D bleaching sequence.

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