Chlorine Dioxide Bleaching of Mixed Hardwood Pulps

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ABSTRACT

In this paper, we report the results of bleaching of mixed hardwood pulps with chlorine dioxide and the synergistic effect of chlorine and chlorne-dioxide in the chlorination stage. In conformity with the expectation, the C.E.D. sequence gives a much better pulp than C.E.H. sequence. It is also noticed that the substitution of chlorine dioxide for chlorine in the first stage of bleaching in the C.E.D. sequence has much less marked effect compared to the one observed in the C.E.H. sequence. In general, the substitution has a synergistic effect leading to increased brightness, viscosity. strength properties and lesser colour reversion of final bleached pulp. It is alsoobserved that the chlorine dioxide has no beneficial effcct on deresination as has been observed by Rapson and co-workers for certain Canadian woods. The possible causes for these are analysed.

In general, all pulps diminish in brightness with age. This brightness revcrsion has been attributed to nearly every constituent of pulp, namely—lignin, hemi celluloses, extractives (resin), metal ions etc. and the method of bleaching. However, only in the recent past, a clear understanding of the important variables controlling brightness reversion has emerged. These developments have been reviewed by Rapson and Spinner[1].

It has now been well established that use of chlorine-dioxide in bleaching results in pulps with higher brightness, lesser colour reversion and considerably increased strength properties. In delineating the mechanism of action of chlorine- dioxide to produce pulps with lesser colour reversion, two factors have generally been recognised.

1. Better deresination of the pulp by the use of chlorine dioxide, as extractive components are known to be contributors to colour reversion[2]. In their studies of chlorine-dioxide bleaching of Canadian Wood Pulps, especiall spruce and birch, Rapson and Co-workers have found-out that the resin content after alkali extraction stage, at constant conditions of deresination decreased with increasing replacement of chlorine by chlorine-dioxide in the chlorination stage, the colour reversion also following the same pattern.

2. Presence of fewer carbonyl and carboxyl groups in the pulps bleached with chlorine dioxide, as this bleaching agent preferentially attacks the lignin and not cellulose[3].

We report in this paper, the results of our investigations on the chlorine dioxide bleaching of mixed hard wood pulps. The results, especially of the brightness reversion aie examined in terms of the two factors, outlined above.

Chlorine dioxide was substituted for chlorine (1 mole of Clo_2 is equivalent to 2.5 moles of chlorine) in the first stage of conventional sequence C.E.H A comparison was also made with C.E.D. sequence. The results of the study are presented in Tables 1 to 5.

From the perusal of the results, the following facts emerge :

1. There is no appreciable reduction in the resin (extractives) percentage, either by replacement of chlorine by chlorine-dioxide in the initial chlorination stage or hypochlorite by chlorine dioxide in the final stage of bleaching.

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TABLE—1
BLEACHING OF MHW PULP OF K. No. 19.2

	Particulars	CEH	C/D_{10} EH	C/D_{20} EH	C/D_{30} EH	C/D_{50} EH	C/D_{70} EH
I.	**Chlorine stage :**						
	a. pH Initial/End	2.25 / 2.05	2.00 / 1.95	1.95 / 1.80	2.25 / 2.00	2.60 / 2.40	2.95 / 2.85
	b. Chlorinated pulp K. No.	7.8	7.2	6.5	6.1	6.1	6.1
	c. Chlorinated pulp viscosity, Cps.	8.5	14.3	14.2	14.1	14.2	14.4
II.	**Alkali Extraction stage :**						
	a. pH initial/End	11.25 / 11.00	11.20 / 11.05	11.10 / 11.00	11.10 / 11.10	11.00 / 11.00	11.3 / 11.0
	b. Alkali consumption %	0.90	0.49	0.49	0.40	0.35	0.34
	c. Extracted Pulp K. No.	5.2	4.5	4.0	3.7	3.6	3.5
	d. Extracted pulp viscosity, Cps.	8.0	13.2	13.5	13.7	14.0	14.1
III.	**Hypochlorite stage :**						
	a. Hypo as Cl_2, %	2.85	2.35	2.35	2.35	2.35	2.35
	b. Buffer as NaOH, %	0.90	0.76	0.78	0.83	0.76	0.81
IV.	**Bleached pulp properties :**						
	a. Brightness %	78.2	79.0	79.0	79.2	78.8	78.0
	b. P.C. No. (16 hrs.)	6.5	6.3	5.2	5.4	5 3	4.8
	c. Viscosity, Cps.	6.2	7.0	7.3	7.5	7.5	9.1
	d. A-B Extractives %	0.68	0.68	0.70	0.67	0 73	0.72
	e. α—Cellulose %	88.4	91.0	90.7	93 0	92.5	92.6
	f. β—Cellulose %	10.1	7.6	8.5	6.5	6.9	7.0
	g. γ—Cellulose %	1.5	1.4	0.8	0.5	0.6	0.4
	h. Copper Number	1 21	0.97	0 91	0.74	0 64	0.56
	i. Ash %	1.07	1.12	0.96	1.14	1.08	1.30

TABLE—2
BLEACHING OF MHW PULP OF K. No. 19 2

	Particulars	CEH	CED	C/D_{10} ED	C/D_{20} ED	C/D_{30} ED
I.	**Chlorination stage :**					
	a. pH Initial/End	2.25 / 2.05	2.10 / 1.95	2.20 / 2.05	2.20 / 2.00	2.25 / 2.00
	b. Chlorinated pulp K. No.	7.8	7.7	7.2	6.5	5.9
	c. Chlorinated pulp viscosity Cps.	8.5	8.5	14.5	14.2	14.3
II.	**Alkali Extraction stage :**					
	a. pH Initial/End	11.25 / 11.00	11.00 / 10.9	11.40 / 11.10	11.10 / 11.00	11.0 / 11.0
	c. Alkali consumption, %	0.90	0.81	0.60	0 57	0 50
	Extracted pulp, K. No.	5.2	5.3	4.6	4.3	3.5
	Extracted pulp viscosity Cps.	8.0	7.7	13.7	13.9	14 0
III.	**Hypochlorite/Chlorine-dioxide stage :**					
	a. Hypo/Clo_2 as Cl_2 %	2.85	2.68	2.70	2.82	2.71
	b. Buffer as NaOH %	0.90	1.22	1.26	1 38	1.14
IV.	**Bleached pulp properties :**					
	a. Brightness %	78.2	78.8	79.0	79 2	79.5
	b. P.C. No. (16 hrs.)	6.5	5.7	5.0	4.0	2 9
	c. Vscosity, Cps	6 2	8.0	10.3	12.7	12 2
	d. A—B extractives %	0.68	0 77	0.72	0.76	0 63
	e. α—Cellulose %	88.4	89.8	92 9	94.5	94 7
	f. β—Cellulose %	10.1	9 5	6 6	5.0	4.9
	g. γ—Cellulose %	1.5	0.7	0.5	0.5	0.4
	h. Copper Number	1.21	1 03	0.75	0.73	0.62
	i. Ash %	1.07	0.32	0.39	0 36	0.38

TABLE—3

BLEACHING CONDITIONS ADOPTED

	Bleaching stage	Consistency %	Chemical %	Temp °C	Retention time hrs.
1.	Chlorination	3.0	6.65 as Cl_2	30±1	1.0
2.	Alkali Extraction	8.0	2.5*; 2.0**	60—65	1.5
3.	Hypochlorite	10.0	—	40—45	2.5
4.	Chlorine - dioxide	8.0	—	70—75	2.0

* CEH sequence

** C/D^{EH} and CED sequence

TABLE—4

STRENGTH PROPERTIES OF BLEACHED PULPS AT 40° SR.

	Particulars		CEH	C/D_{10} EH	C/d_{20} EH	C/D_{30} EH	C/D_{50} EH	C/D_{70} EH
i.	Burst Index	KPa m^2/g	2.71	2.91	3.28	3.20	3 28	3.24
ii.	Tear Index	mN m^2/g	4.02	4.90	4.70	4.60	4.61	5.0
iii.	Breaking length	km.	5.95	6.35	6.75	6.25	6.30	6.41
iv.	Double folds	No.	4	9	12	15	19	16

TABLE—5

STRENGTH PROPERTIES OF BLEACHED PULPS AT 40°SR

	Particulars		CEH	CED	C/D_{10} ED	C/D_{20} ED	C/D_{30} ED
i.	Burst Index	KPa m^2/g	2.71	2.96	3.69	3.31	3.46
ii.	Tear Index	mN m^2/g	4.02	5.60	6.76	6.86	6.47
iii.	Breaking Length	km.	5.95	6.00	6.36	6.61	6.40
iv.	Double Folds,	No.	4	15	57	40	47

2. Replacement of chlorine by chlorine-dioxide in any stage of bleaching results in lesser brightness reversion as seen by lower post colour number values.
3. Increased use of chlorine-dioxide results in pulps of lower copper number.
4. Use of chlorine-dioxide results in pulps of higher strength.

Thus, it is evident from the results that the main factor responsible for the brightness reversion in the case of mixed hardwood pulps, similar to that of Bamboo pulps is the formation of carbonyl and carboxyl and carboxyl functions of cellulose. Deresination plays only a minor role as seen by the fact that there is very little Changes in extractives content although the post colour number changes markedly. The response of tropical mixed hardwood pulps is thus in contrast to that of pulps of Canadian Woods studied by Rapson and Co-workers. It is also seen that chlorine-dioxide treatment has little effect on the removal of extractives during the bleaching of tropical hardwood pulps.

It will also be pertinent to refer to the observations of Mac Millan and Rapson[5] and Virkola, Hentola and Sihtola[6], who have found an approximate linear relation between brightness reversion and copper number for the periodate treated cotton linters pulp and the copper number is normally related to the presence of reducing groups like Keto groups.

The improvement in strength properties with chlorine-dioxide bleaching can be traced to the fact that the chlorine-dioxide selectively delignifies without causing cellulose degradation, which is one of the controlling factors of stregth properties. Similar increases in strength properties have been observed in the case of bleaching of bamboo pulps also[7,8]

EXPERIMENTAL :

Chlorine-dioxide was generated in the laboratory using a reaction mixture of sodium chlorate (180 gms./liter) and sodium chloride (100 gms/liter) solutions as explained in our earlier paper[7].

For each batch of unbleached mixed hardwood pulp, the optimum amount of chlorine for the chlorination was determined. Then ohlorine dioxide was substituted for an equivalent amount of chlorine, the other conditions being maintained constant, in different proportions in the chlorination stage of both C.E.H. and C.E.D. sequences. The final bleached pulps after thorough washing were tested for their brightness, post colour number (16 hrs.), strength properties at 40° SR after beating in valley beater, and chemical properties as per TAPPI standard methods.

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