In Plant Colour Reduction of the Bleach Plant Effluent

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A novel method of bleaching of bamboo and blends of bamboo and hardwood sulphate pulps is described which enables to reduce the colour of the bleach plant effluent by 75-80%. The sequence consists of chlorination-unbuffered hypochlorite-combined extraction plus hypochlorite i. e., C/H/EH/H. When bleaching pulps of $KMnO_4$ No. 23-25, by this sequence, the available chlorine consumption as hypochlorite is increased by about 1.5%, and caustic soda reduced by about 0.75% (on pulp) when compared to where C/E/H/H sequence is followed.

Introduction

The presence of colour in the effluent of pulp mills, in addition to giving aesthetic problems, can interfere with biological activity by retarding transmission of sun light into water. The main contributors to colour of the effluent, are the wastes from the bleach section and in this case also the caustic extraction stage effluent exhibits the maximum colour. Since the seriousness of the problem has been realized all over the world, methods are developed to remove the colour. The chemical treatment methods consist in using hydrated lime, alum, ferric sulphate, ferric chloride etc. Adsorption with activated carbon or polymeric resins is also reported. However, any of these treatment methods involve substantial expenditures of capital and operating costs which at present in the Indian Pulp and Paper Industry mny be considered economically prohibitive. It is this consideration which prompted us to develop a bleaching sequence, which will reduce the colour of the effluent in the bleaching process itself.

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It is reported that some mills in U. S. A. in order to reduce the colour of the bleach plant effluent are using C/H/E/H sequence over C/E/H/H. A comparative study of these two sequences was earlier carried out[1] and since the total colour produced was nearly same, this was not considered for further experiments. The sequence C/H/E/H with suitable modification enabled to reduce the colour to the extent of 75-80 % and the present paper describes these findings.

EXPERIMENTAL :

Colour measurement

A stock standard platinum cobalt solution was prepared having a colour of 500 units by dissolving 1.246 grams of potassium chloroplatinate K_2PtCl_6 (equivalent to 0.500 gm metallic platinum) and 1 gram crystallized cobaltous chloride $COCl_2.6H_2O$ (equivalent to about 0.25 gm metallic cobalt) in distilled water with 100 ml conc. HCl and diluting to 1 litre with distilled water. By diluting this solution, solutions of different colour units were obtained. The absorption of these solutions were noted on Uvispek Spectrophotometer at a wave lengh of 400 mμ. The absorption were plotted against the colour units. To determine the colour of the effluent the absorption values were transferred to the platinum cobalt units with the help of calibration curve. (Standard methods for the examination of water and waste water, 12th ed., Am. Publ. Health. Ass. Inc., New York 1965).

The colours of the effluents from each of the stages are for undiluted effluents, and were measured at the prevailing pH values. After mixing the individual effluents of the E/H/H and H/EH/H stages in equal proportion the colours were recorded at the pH obtained for the mixed effluent. The pH has varied a little and is on the lower side for the effluent from H/EH/H sequence. Since colour

is sensitive to pH, the colour of the mixed effluent was recorded at pH 7 also and the results are given in table VII.

For all bleaching experiments, chlorinated pulps were collected from the chlorine washer on different days from the bleach plant. The pulps were not subjected to any further washing and were used as such, after ascertaining the consistency and weighing the required amount, for further bleaching experiments. The chlorinated pulps of the plant are never thoroughly washed free of hydrochloric acid and soluble chlorolignins and it was found that 0·5% caustic soda on pulp is required for neutralization because of incomplete washing. In all hypochlorite stages a clear solution of calcium hypochlorite containing 30 g. p. l. av. Cl_2 and 1.0 g. p. l. $Ca(OH)_2$ was used.

Results & Discussion

The sequence C/H/EH/H was developed in stages. Initial experiment using sequence C/H/EH/H showed that a light coloured (visual observation) effluent will be obtained, at increased hypochlorite consumption, but reduced caustic consumption, when compared to where C/E/H/H sequence is used (Table I). Based on this result another set of experiments was carried out, wherein the savings in the caustic and increase in hypochlorite consumption were determined for the sequence C/H/EH/H. The comparative effectiveness of the C/EH/H/H sequence in producing a light coloured effluent was also determined for comparison with C/ E / H / H and C / H / EH / H sequences. The results show that the sequence C/H/EH/H has the distinct advantage of producing a less coloured effluent over C/E/H/H or C/EH/H/H.(TableII). It has the additional advantage over C/E/H/H sequence in that the caustic consumption is reduced about 0.75% for the constant end pH, but the disadvantage of increasing the available chlorine consumption by about 1.5% (on pulp). Since C/H/EH/H and C/EH/H/H sequences compared in their values for chlorine consumption, the points in favour of C/H/EH/H sequence were reduced colour, reduced caustic consumption. However the results in both the table I and II gave an indication that

TABLE I

Bleaching of Chlorinated Pulp Using Sequences E/H/H and H/EH/H

E/H/H		H/EH/H	
Extraction		*Hypochlorite*	
NaOH on pulp, %	2.25	Av. Cl_2 on pulp, %	2.0
End pH	8.6	Cl_2 consumed, %	2.0
		End pH	2.7
Hypochlorite		*Extrabtion + Hypochlorite*	
Av. Cl_2 on pulp, %	3.0	NaOH on pulp, %	2.25
Cl_2 consumed, %	2.62	Av. Cl_2 on pulp, %	1.25
End pH	7.0	Cl_2 consumed, %	1.25
		End pH	10.3
Hypochlorite		*Hypochlorite*	
Av. Cl_2 on pulp, %	1.25	Av. Cl_2 on pulp, %	2.5
Cl_2 consumed, %	0.49	Cl_2 consumed, %	1.8
End pH	7.8	End pH	7.7
Total Cl_2 added, %	4.25	Total Cl_2 added, %	5.75
Cl_2 consumed, %	3.11	Cl_2 consumed, %	5.05
Brightness of pulp, % (Elrepho)	79.2	Brightness, %	80.6
Viscosity, cp, (CED)	13.6	Viscosity, cp, (CED)	11.3

	E	H	H	H	EH	H
Consistency, %	5	5	5	5	5	5
Temp., °C	60	45	45	45	45	45
Time, Min.	60	60	90	60	60	90
Sulphamic acid on pulp, %	...	0.07	0.07	...	...	0.07

TABLE—II Bleaching of Chlorinated Pulp Using Sequences E/H/H, EH/H/H and H/EH/H

Extraction	E/H/H	*Extraction + Hypochlorite*	EH/H/H	*Hypochlorite*	H/EH/H
NaOH on pulp, %	2.25	NaOH on pulp, %	2.25	Av. Cl_2 on pulp, %	2.0
End pH	8.8	Av. Cl_2 on pulp, %	1.75	Cl_2 consumed, %	2.0
Colour,		Cl_2 consumed, %	1·75	End pH	2·7
Pt. Co. Units	6900	End pH	8.0		
		Colour, Pt. Co. Units	2520		
Hypochlorite		*Hypochlorite*		*Extraction + Hypochlorite*	
Av. Cl_2 added, %	3.0	Av. Cl_2 added, %	3.0	NaOH on pulp, %	1.5
Cl_2 consumed, %	2.68	Cl_2 consumed, %	2.50	Cl_2 added, %	1.5
End pH	7.1	End pH	7.5	Cl_2 consumed, %	1.5
				End pH	8.9
				Colour, Pt. Co. units	1350
Hypochlorite		*Hypochlorite*		*Hypochlorite*	
Av. Cl_2 added, %	1.0	Av. Cl_2 added, %	1.0	Cl_2 added, %	2.0
Cl_2 consumed, %	0.5	Cl_2 consumed, %	0.42	Cl_2 consumed, %	1.36
End pH	7.5	End pH	7.7	End pH	7.6
Total Cl_2 added, %	4·0		5.75		5.5
Cl_2 consumed, %	3.18		4.67		4.86
B-ightness, % (Elrepho)	78.8		78.6		77.8
Viscosity, cp, (CED)	15.2		14.8		12.3

	E	H	H	EH	H	H	H	EH	H
Consistency, %	5	5	5	5	5	5	5	5	5
Temp., °C	60	45	45	60	45	45	45	45	45
Time, Min.	60	60	90	60	60	90	60	60	90
Sulphamic acid on pulp, %	...	0.07	0.07	...	0.07	0.07	...	...	0.07

TABLE—III Bleaching of Chlorinated Pulp Using Sequences E/H/H and H/EH/H

	E/H/H		H/EH/H
Extraction		*Hypochlorite*	
NaOH added, %	2.25	Cl_2 added,%	2.25	1.75
End pH	8.5	Cl_2 consumed, %	2.17	1.69
Colour, Pt. Co. units	7500	End pH	3.0	2.7
		Colour, Pt. Co. units	210	205
Hypochlorite		*Extraction + Hypochlorite*		
Cl_2 added, %	3.0	NaOH added, %	1.5	1.5
Cl_2 consumed, %	2.84	Cl_2 added, %	1.25	1.75
End pH	6.6	Cl_2 consumed, %	1.25	1.75
Colour, Pt. Co. Units	360	End pH	8.8	8.5
		Colour, Pt. Co. units	1375	1300
Hypochlorite		*Hypochlorite*		
Cl_2 added, %	1.00	Cl_2 added, %	2.0	2.0
Cl_2 consumed, %	0.58	Cl_2 consumed, %	1.34	1.38
End pH	7.2	End pH	7.3	7·1
Colour, Pt. Co. Units	60	Colour, Pt. Co. units	85	95
Total Cl_2 added, %	4.0		5.5	5.5
Cl_2 consumed, %	3.4		4.76	4.82
Brightness, % (Elrepho)	78.6		78.6	78.6
Viscosity, cps (CED)	13.6		12.8	13.2
Combined colour mixed in equal proportion (1:1:1)	2200		500	450
E/H/H or H/EH/H	(pH 6.9)		(pH 6.4)	(pH 6.0)

Constant Conditions .	E	H	H	H	EH	H
Temp,. °C	60	45	45	35	45	45
Time, Min.	60	60	90	60	60	90
Sulphamic acid on pulp, %	...	0.07	0.07	0.07	...	0.07

TABLE—IV

Bleaching of Chlorinated Pulp Using Sequences E/H/H and H/EH/H

	E/H/H			H/EH/H	
Expt. No. :–	1	2		1	2
Extraction			*Hypochlorite*		
NaQH added, %	3.0	2.5	Cl_2 added, %	2.00	1.75
End pH	9.6	8.4	Cl_2 consumed, %	1.91	1.69
			End pH	3.0	2.7
Colour, Pt. Co. Units	9000	8500	Colour, Pt. Co. units	230	275
Hypochlorite			*Extraction + Hypochlorite*		
Cl_2 added, %	3.0	3.25	NaOH added, %	2.25	1.75
Cl_2 consumed, %	2.74	2.74	Cl_2 added, %	1.5	1.75
End pH	6.9	7.2	Cl_2 consumed, %	1.5	1.75
			End pH	9.5	8.3
Colour, Pt. Co. Units	330	290	Colour, Pt. Co. Units	2050	2000
Hypochlorite			*Hypochlorite*		
Cl_2 added, %	1.0	1.5	Cl_2 added, %	2.0	3.0
Cl_2 consumed, %	0.54	0.63	Cl_2 consumed, %	1.49	2.0
End pH	7.4	7.7	End pH	7.3	7.7
Colour, Pt. Co. Units	50	100	Colour, Pt. Co. units	85	80
Total Cl_2 added, %	4.00	4.75		5.5	6.5
Cl_2 consumed, %	3.28	3.37		4.90	5.44
Brightness, % (Elrepho)	77.3	78.3		75.4	78.4
Viscosity, cp, (CED)	11.4	14.5		11.0	13.5
Total colour, Pt. Co. Units	9380	8890		2365	2355

Constant conditions same as in Table III

for the conditions used, the viscosity of the pulp obtained using C/H/EH/H sequence were a little on the lower side when compared to where C/E/H/H sequence was used. This gave a clue that suitable modification in the conditions will have to be done in the first unbuffered hypochlorite stage, where the end pH was about 2·7. The following changes were introduced viz. temperature was reduced to 35°C from 45°C and 0.07% sulphamic acid on pulp was added. The purpose of reducing the temperature and incorporating the use of sulphamic acid was to make the conditions milder and to carryout the unbuferred hypochlorite stage in the presence of a protector i. e., sulphamic acid (Table III). This improved the viscosity of the pulp, to nearly the same level as that obtained when using C/E/H/H sequence. These results were further confirmed (Table (IV) by bleaching two different chlorinated pulps (Exp. No. 1 and 2) by C/E/H/H and C/H/EH/H sequence Further in these experiments under the conditions studied it was established that 0.75% caustic soda (on pulp) will be saved for an increase in chlorine con-

Table–V

Physical Strength Characteristics of the Standard Handsheets

	Bleaching sequence C/E/H/H. Pulps of Exp. No. 2 (Table IV)				Bleaching sequence C/H/EH/H Pulps of Exp. No. 2 (Table IV)			
	1	2	3	4	1	2	3	4
Freeness, °SR	25	40	50	59	24	39	48	58
Drainage time, Sec.	13	35	55	80	13	32	53	76
Basis Wt., g/m²	60.0	60.7	59.5	59.6	59.0	58.8	58.8	58.5
Thickness, microns	107	98	93	89	105	98	93	88
Bulk, cc/g.	1.78	1.65	1.56	1.49	1.78	1.67	1.58	1.50
Double folds (MIT)	20	47	89	129	17	49	98	113
Tear factor	81.7	71.0	67.3	63.0	83.0	73.0	69.5	63.9
Breaking length, km	3.16	4.12	4.60	5.46	3.03	4.04	4.88	5.97
Burst factor	29.0	36.6	40.4	43.6	28.7	37.4	40.7	42.7
Bendtsen Porosity, ml/min.	2400	530	190	70	2600	550	200	90
P. C. No.	5.48	—	—	—	5.10	—	—	—
Viscosity, cp, (CED)	14.5	—	—	—	13.5	—	—	—

*Drainage time was determined in the British Sheet making machine

Table VI

Comparative Bleaching Data for C/E/H/H and C/H/EH/H Sequences, Using 10% Consistency During Bleaching

	C/E/H/H		C/H/EH/H
Extraction		*Hypochlorite*	
NaOH added, %	2.75	Cl_2 added, %	1.75
End pH	9.6	Cl_2 consumed, %	1.70
Colour, Pt. Co. Units	16000	End pH	2.5
		Colour, Pt. Co. Units	350
Hypochlorite		*Extraction+Hypochlorite*	
Cl_2 added, %	3.0	NaOH added, %	2.0
Cl_2 consumed, %	2.66	Cl_2 added, %	1.75
End pH	7.1	Cl_2 consumed, %	1.75
Colour, Pt. Co. Units	380	End pH	9·5
		Colour, Pt. Co. Units	1650
Hypochlorite		*Hypochlorite*	
Cl_2 added, %	1.0	Cl_2 added, %	2.0
Cl_2 consumed, %	0.58	Cl_2 added, %	1.46
End pH	7.6	End pH	7.3
Colour, Pt. Co. Units	75	Colour, Pt. Co. Units	100
Total Cl_2 added, %	4.0	...	5.5
Cl_2 consumed, %	3.24	...	4.91
Total colour, Pt. Co. Units	16455	...	2100
Brightness, %	80.0	...	78.8
Viscosity, cp	11.6	...	10.7
Unbld. K. NO.	23-25	...	23-25

Constant Conditions

	E	H_1	H_2	E	H_1	H_2
Temp., °C	60	45	45	35	45	45
R. T., Min.	60	60	90	60	60	90
Cy., %	10	10	10	10	10	10
Sulphamic acid on pulp, %	...	0.07	0.07	0.07	...	0.07

Note : Chlorinated pulp collected from the plant and subjected to E/H/H and H/EH/H bleaching. (Bamboo pulp : Wood pulp=70:30).

sumption to the extent of 1.5–1.7% when C/H/EH/H sequence is followed. The colour of the effluent will be also less by about 75% when compared to where C/E/H/H sequence is followed. The results of viscosity and physical strength characteristics of standard handsheets (Table V) have confirmed that there will be no lowering in pulp quality when C/H/EH/H sequence is followed. Since some mills practice bleaching at 10% consistency, the comparative effectiveness of C/E/H/H and C/H/EH/H sequences was determined for another chlorinated pulp collected from the plant. The indications were the same viz. significant reduction in the colour was obtained with reduced caustic consumption and increased hypochlorite consumption, when C/H/EH/H was followed. The viscosity of the pulp was 10.7 cp compared to 11.6 cp obtained using C/E/H/H sequence.

An important point which transpired during these experiments was that using C/H/EH/H sequence the chlorine consumption as hypochlorite was more by about 1.5% compared to where C/E/H/H sequence is followed. This necessitated that if this amouut of chlorine is added separately for decolurising the caustic extraction stage effluent of the C/E/H/H sequence, what will be its effectiveness ? It was found that this method of reducing the colour of the effluent was not as effective as obtained in C/H/EH/H sequence. Further when hypochlorite was added to the caustic extract, many times precipitation was also observed, obviously because of the reaction of soluble lime present in hypochlorite with the colur bodies present in caustic extract. For this consideration also the favourable sequence for reducing the colour of the bleach

TABLE VII : PH and Colour of Individual Effluents and Mixed Effluents

Sl No.	Bleaching sequences E/H/H Effluent sample	Initial pH	Final pH	Colour Pt. Co.Units at the final pH	H/EH/H Effluent sample	Initial pH	Final pH	Colour Pt. Co Units at the final pH
1	E Stage	8.5	8.5	6800	H Stage	2.3	2.3	215
2	H_1 Stage	7.0	7.0	380	EH Stage	8.7	8.7	1550
3	H_2 Stage	7.5	7.5	60	H Stage	7.6	7.6	90
4	Mixed Effluent (E:H:H = 1:1:1)	6.8	6.8	2100	Mixed Effluent (H:EH:H = 1:1:1)	5.2	5.2	410
5	Mixed Effluent (E:H:H = 1:1:1)	6.8	7.0*	2150	Mixed Effluent (H:EH:H = 1:1:1)	5.2	6.8*	450
6.	—	—	—	—	Mixed Effluent (H:EH:H = 1:1:1)	5.2	7.0*	480
7					H Stage	2.3	7.0*	525

* pH was raised by adding caustic soda

plant effluent was finally C/H/EH/H.

The data for the colour of the effluents obtained in E/H/H and H/EH/H bleaching stages for a chlorinated pulp collected from the plant is recorded in Table VII. The results show marked difference in the colour of the effluent obtained using E/H/H and H/EH/H bleaching sequence, and after adjusting the pH to 7 by caustic soda the latter is lighter by about 80%.

Conclusions

(1) Substantial reduction in the colour of the bleach plant effluent can be obtained using C/H/EH/H sequence.

(2) Pulp quality is equivalent to that from the C/E/H/H sequence.

(3) In mills which have already facilities for primary and secondary treatment and where effluent colour remains a problem, this restructured conventional bleaching sequence possesses high economic potential.

(4) The reduction in colour can be obtained with existing bleach plant chemicals and also existing bleach plant epuipment.

(5) Since all the bleaching stages are carried out at 35-45°C, steam savings will be effected.

(6) The cost of the bleaching chemicals will be nearly equivalent to that of the control.

(7) In the H/EH/ stage increased foaming tendency was observed, and its effect has to be evaluated in the plant trials.

References

1. Unpublished work, Research Centre, The West Coast Paper Mills Ltd.