Bleaching of High K. No. Bamboo Sulphate Pulp By Chlorine Dioxide

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High permanganate number (22-28) bamboo sulphate pulps are bleached using chlorine dioxide to get high brightness with minimum degradation of pulp. The most efficient methods of lignin removal like the use of mixture of chlorine and chlorine dioxide in the first stage, and the sequential addition of chlorine dioxide before the application of chlorine are also studied,

It is found that the bamboo pulp can be bleached to 83-84% brightness in three stages C/EH/D using about 0.6-0.8% chlorine dioxide on pulp basis. The bamboo pulp obtained is comparable in all respects except tear with the imported "PUGET" bleached pulp. The use of chlorine dioxide is beneficial after about 70% brightness i.e. after C/E/H or C/EH/ stages.

The commonly used sequences like C/E/H/D/E/D, C/E/C/E/H/D, C/EH/D/E/D, C/EH/H/D/E/D, CD/E/H/D/E/D, etc. are studied. By these sequences it is possible to get about 88-89% brightness. The ceiling point of brightness for the bamboo sulphate pulp of high permanganate numbers appears to be 89%.

The bleaching and purification of chemical pulps have always been carried out with chlorine or chlorine containing compounds. Elemental chlorine and hypochlorites have been the most important chemicals used because of their economy, and ability to bleach and purify the pulps. Purification is easily affected to a large degree by chlorination followed by caustic extraction without excessive damage to pulp. Bleaching of the colouring matter, and destroying the final traces of lignin, however, have been more difficult to accomplish without causing damage to the pulp (1). The hypochlorites are universally used to bleach the pulp, even though they cause damage to cellulose. Moreover, the hypochlorite bleaching introduces the carbonyl group in the cellulose chain which increases the colour reversion of the pulp (2).

On the other hand, chlorine dioxide has got specific action towards lignin and the colouring matter. It is a very efficient bleaching agent in removing the last traces of lignin and boosting the brightness of pulp considerably (3). It does not attack the carbohydrate fraction when used under controlled conditions. Higher strength and higher brightness can be achieved by chlorine dioxide with excellent brightness stability.

Inspite of ample evidence that chlorine dioxide is a splendid chemical for bleaching chemical pulps, its commercial use was retarded by the difficulty in its manufacture and its high cost. The commercial bleaching by chlorine dioxide was started in about 1946 in Sweden. Since then efforts are being made to generate chlorine dioxide as cheap as possible and to eliminate all possible hazards during the manufacture. In recent years, the difficulties are almost overcome and chlorine dioxide has replaced hypochlorite in many mills. In some localities of Canada, chlorine dioxide is cheaper than hypochlorite on equal chlorine basis (4). Amongst the many manufacturing methods of chlorine dioxide the R-2 process developed by WH Rapson is the best, considering the cost, easy operation and producing the mixture of chlorine and chlorine dioxide in desired proportions. Recently Rapson (5) has proposed a new chemical supply system for a craft mill having R2-process for chlorine dioxide manufacture, which simplifies to a great extent the handling of chemicals and reduces the cost of bleached pulp. In this system almost all the oxidising value of unbleached pulp can be met. The mixture of chlorine dioxide replaces all chlorine in the first stage, and excess white liquor produced by sodium sulphate (a byproduct of R2-process) can be used in the caustic extraction stage replacing the caustic soda. The chlorine dioxide is used for further bleaching. The great advantage of the R2-process is the excellent versatility of production of chemicals, such as desired mixture of chlorine and chlorine dioxide, and sodium sulphate by employing sodium chloride, sodium chlorate and sulphuric acid in the process.

These significant developments coupled with the advantages of chlorine dioxide stimulated the complete replacement of hypochlorite and extensive use of chlorine dioxide in first stage along with chlorine.

The chlorine application in the first stage was considered to be the best for the removal of major amount of lignin in chemical pulps all these years. But a bet-

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ter delignification of chemical pulp was announced for the first time in 1959 where a small amount of chlorine dioxide with chlorine was used in chlorination stage. Later it was confirmed that the use of a mixture of chlorine dioxide and chlorine in the first stage increased the viscosity of pulp after subsequent bleaching, compared to where only chlorine was used.

Furthes, the mill tsials with the use of chlorine and chlorine dioxide mixture in the first stage showed the following merits over the use of chlorine (i) more efficient lignin removal (ii) less degradation of pulp (iii) Higher and stable brightness and (iv) greater strength of pulp (6).

The reaction mechanism for the above effects is not clearly understood. But it is clear that there is a synergistic effect.

The optimum ratio of chlorine to chlorine dioxide in the first stage was studied systematically by Rapson and Anderson (7). The result of their study showed that the optimum ratio of chlorine to chlorine dioxide was 30 : 70 or 40 : 60 where maximum delightfication takes place.

A very significant advance has been recently made by Hooker Chemicals Limited in the use of chlorine dioxide in the first stage bleaching. This is known as "Sequential addition" and represented by Dc. It consists in the application of chlorine dioxide to unbleached pulp in an amount (Y) at low consistency and temperature and reacting for a suitable period of time. The (Y) is less than the equivalent amount of chlorine (X) which is the optimum demand in the chlorination stage. Then without washing the pulp, the chlorine (X — Y) is applied and further chlorination is carried out as usual.

The chlorine to chlorine dioxide ratio may be varied but best results are obtained between the ratios of 40 : 60 and 60 : 40 the chlorine dioxide expressed as chlorine (8). The chlorine dioxide reaction time may be from 3-30 minutes or more, and the chlorination time may be from 5-60 minutes. The washing in between two stages produces slightly lower brightness and is not beneficial.

JV. Hatton had studied tse sequential addition Dc and compared it with the use of mixture CD. Both methods are used to delignify the pulp without much degradation and substantial saving in caustic soda is achieved in both cases.

The study also revealed that there is a superior delignification as measured by the permanganate number in the case of sequential addition than the mixture for the same amount of total chlorine. For the same degree of delignification the chlorine dioxide required is less in the sequential addition than in the case of mixture.

The same author, Hatton (9) studied further about the oxidant demand. He studied the colour stability, total chlorine consumption and caustic soda saving by studying C,CD, Dc in the first stage in a 3, 4 and 6 bleaching stages.

The optimum oxidant levels of the pulp in the first stage in C, CD and Dc were 1.13, 1.20 and 1.20 Roe number for a retention time of one hour.

The colour reversion of semi and fully bleached pulps increase in the order Dc, CD, C. Generally the viscosities are higher by about 30-33% by sequential addition compared to conventional method. The permanganate number of the pulp varies continuously in the process and it is difficult to predict the optimum chlorine demand exactly. But in the case of sequential addition and mixture, even if the amount of addition exceeds the optimum demand, there is no harm.

Tne overall soperiority of the sequential addition of chlorine dioxide and chlorine is established in delignification over any other known methods. A tentative explanation has been proposed for the enormous synergistic effects prevailing in the sequential treatment and to a lesser extent in the mixture treatment. The explanation is based on the hypothesis that the relatively slower and predominently oxidative attack on lignin by chlorine dioxide is very efficient and thereby suitably "Activates" the remaining lignin for the subsequent chlorine treatment.

At present in India no paper mill is bleaching the paper grade pulp by chloring dioxide. This is largely due to the high cost of chlorine dioxide and lack of know-how. Almost all mills have the C/E/H/ sequence due to the low cost, even though, the final pulp is degraded by hypochlorite and there is a considerable colour reversion of pulp. But in future, these mills will have to switch over to the use of chlorine dioxide in their bleaching system to get pulps of high brightness and strength with acceptable colour stability.

In our earlier report (10) the bleaching of the high permanganate number bamboo sulfate pulp by chlorine, caustic soda and hypochlorite was discussed. And also a study was made about the beneficial use of sulfamic acid and sodium silicate during bleaching.

The present paper deals with the bleaching of the high K.No. (22 to 28) bamboo bleached sulfate pulp by chlorine dioxide, using different bleaching sequences. The use of mixture of chlorine and chlorine dioxide in the first stage and the sequential additions of chlorine dioxide before chlorination are also studied for the bamboo pulp.

EXPERIMENTAL

A number of experiments were carried out in the Central Laboratory of the West Coast Paper Mills Ltd., Dandeli (North Kanara) to bleach bamboo sulfate pulp by various sequences. This study could be divided into three parts.

Part I The chlorine dioxide was applied after C/E, and C/EH/ stages.

Part II The mixture of chlorine and chlorine dioxide was used in first stage and few bleaching sequences were studied.

Part III Sequential addition of chlorine dioxide was studied on bamboo sulfate pulp which is a recent and promising method of delignification.

Bleaching of High K.No. Bamboo Sulphate Pulp by Chlorine Dioxide

For these studies the unbleached screened bamboo pulp from pulp mill was collected. Since the experiments were spread over to a long period, different pulps were used. However, as far as possible, same pulp was used for a set of conditions. The pulps were bleached by different bleaching sequences using chlorine dioxide. The study of colour reversion was not made as there is a less colour reversion in the case of chlorine dioxide bleached pulps (11). The conditions followed in different bleaching stages are given below and they are referred to in this paper as normal conditions.

1 Chlorination

Mixture of chlorine and chlorine dioxide
Consistency, % 3.0
Temperature, 28°C

Retention time, Mts. 60

2 Caustic soda extraction

Consistency, %	5.0
Temperature, °C	50
Retention time, mts.	60
pH	9-5—10.5

3 Calcium Hypochlorite

Consistency, %	5.0
Temperaturt, °C	40
Retention time, mts.	100—150
pH	8.0—9.5

4 Chlorine dioxide

Consistency, %	5.0
Temperature, °C	60
Retention time, mts.	30—240
pH	not controlled

The abbreviations used in this paper for bleaching stages are :

C	Chlorination
CD	Chlorine and Chlorine dioxide mixture
Dc	Sequential addition of chlorine dioxide
E	Caustic soda extraction
H	Calcium hypochlorite
EH	Caustic extraction + hypochlorite

The stroke (/) in between two stages indicates the washing of pulp by water. Wherever chlorine dioxide is applied at the final bleaching stage, the pulp is treated with SO_2 for about 10-15 mts. at pH 4.5—5.0 to remove residual chlorine and to stabilise the brightness of the pulp.

PREPARATION OF CHLORINE DIOXIDE

Chlorine dioxide was prepared in low concentration by Schachert's method (12). This method consisted of heating a finely powdered mixture of sodium chlorate (50 g.) oxalic acid dihydrate (40 g.) and 160 ml. of 33.0% (by vol.) of sulphuric acid at 30—60°C. All glass apparatus was used and effluent of mixture of gases was scrubbed with a saturated solution of sodium chlorite to oxidise any chlorine to chlorine dioxide. The chlorine dioxide gas was absorbed in ice cold water (500 ml.) contained in an amber glass bottle. A reaction period of one hour was sufficient for the evolution of the bulk of chlorine dioxide.

The chlorine dioxide solution analysis (Tappi, monograph No. 10 page 133), brightness of pulp (T217 m-46), Permanganate No. (T 214 m-50), Kappa No. (T 236 m-60) and viscosity of pulp (Cuprammonium CCA 13) were carried out according to standard procedures.

PART I

i The hypochlorite bleaching of pulp invariably degrades the cellulose resulting in poor strength and colour reversion. In this study an attempt was made to bleach the pulp without the use of hypochlorite. The chlorine dioxide was applied to the pulp after the C/E/stage with the expectation of getting good brightness. The bleaching conditions with the results are recorded in Table No. I.

TABLE NO. I

Bleaching of pulp by sequence C/E/D1/D2/

Normal bleaching conditions

Pulp Permanganate No. 22.6

Experiment No. 1

(1)	Chlorination, C	
	Chlorine added, %	10.0
	Chlorine consumed, %	9.8
(2)	Caustic extraction, E	
	Caustii soda added, %	2.5
	Permanganate No.	10.5
(3)	Chlorine dioxide, D1	
	Chlorine dioxide as such applied, %	1.7
	Chlorine dioxide as such consumed, %	1.7
	Retention time, mts.	120
	Brightness, %	57
(4)	Chlorine dioxide, D2	
	Chlorine dioxide as such applied, %	1.7
	Chlorine dioxide as such consumed, %	1.7
	Retention time, hrs.	2.0
	Brightness, %	66

It was clear from the above results that after C/E/ stage where K.No. was 10.5 the application of chlorine dioxide resulted in poor brightness. Almost all chlorine dioxide was consumed and pH was low due to the formation of hydrochloric acid. Again, after washing the pulp when the chlorine dioxide was used there was increase in brightness by only 9 points. Considering the amount of chlorine dioxide applied to pulp, the brightness gain was poor and therefore the sequence is commercially impracticable.

Hence, it was concluded that the use of chlorine dioxide after C/E/stage in this study did not help. But in Western countries the most commonly used sequence is C/E/D/E/D that gives about 88-90% brightness (13). Of course here the pulps are different and the K.No. of bamboo pulp before the application of chlorine dioxide was qoite high—10.5.

ii It is reported (2) that the chlorine dioxide application is beneficial in removing the last traces of lignin thereby boosting the brightness considerably. Accordingly in the next experiments the pulp brightness was increased to about 70 per cent brightness by the C/EH/sequence. The 'EH' stage consisted of adding the hypochlorite in the alkali extraction stage, where extraction and bleaching takes place simultaneously. Afterwards the chlorine dioxide was used. The bleaching results are given in table No. II.

TABLE NO. II

Bleaching of Pulp by Sequence C/EH/D

Normal bleaching conditions

Unbleached pulp K. No. 22.6

Experiment No. 2

(1)	Chlorination, C	
	Chlorine consumed, %	9.0
(2)	Caustic/hypo stage, EH	
	Caustic soda added, %	2.0
	Hypo addedd, %	4.5
	Initial pH	9.0
	Final pH	8.0
	Time, mts.	40
	Brightness, %	69
	Viscosity, cP	46.5
	Permanganate No.	2.7
(3)	Chlorine dioxide stage, D	
	Chlorine dioxide as such added, %	1.5
	Chlorine dioxide as such consumed, %	1.45
	Initial pH	6.8
	Final pH	6.0
	Time, mts.	240
	Brightness, %	83.0
	Viscosity, cP	58.5

The brightness gain was considerable and it was possible to get 83% brightness in three

stages (C/EH/D). In this case pH was not controlled. The pulp viscosity was not affected.

Effect of pH:- A set of experiments were carried out to see the effect of pH during chlorine dioxide stage on the brightness improvement. The chlorine dioxide was applied after C/EH/ stage at different pH by adding normal sulphuric acid. The results are recorded in Table No. III.

TABLE NO. III
Effect of pH during bleaching

Normal bleaching conditions Brightness of C/EH/sequence pulp 69.%				
Experimental Nos.	3	4	5	6
Chlorine dioxide as such added, %	1.56	1.56	1.56	1.56
Chlorine dioxide, as such consumed, %	1.52	1.43	1.42	1.26
Sulphuric acid added	Yes	Yes	Yes	No
Initial pH	3.0	4.2	5.0	7.0
Final pH	2.0	2.5	3.5	6.0
Time, mts.	240	195	180	230
Brightness, %	81.5	84.0	82.5	83.0
Viscosity, cP	69.5	75.0	69.2	58.5

There was no marked effect of pH on brightness of pulp. But there was less chlorine dioxide consumption and less retention time reuired in the pH range of 5-7. It is interesting to note that the viscosity of C/EH/stage pulp was 46.5 cP and after the chlorine dioxide treatment (Expt. No. 3, 4 and 5) the viscosity of pulp is increased to 58.5 — 75.0. This is a significant improvement in viscosity. This may be explained because of the selective action of chlorine dioxide. The longer chain fraction of the pulp is left unaffected, the shorter chain fraction of pulp is dissolved. This increased the viscosity of resultant pulp. Therefore, it stands to reason that if the degradation of pulp during C/E/ and C/EH/ stages is kept lower the pulp will not be degraded any further due to the use of chlorine dioxide. It is not so when hypochlorite is used for bleaching.

Effect of temperature:- The temperature during chlorine dioxide stage was 60°C (i and ii). In the following experiment the temperature was raised to 68°C in order to see whether it improves the brightness of pulp.

TABLE IV
Effect of Temperature during bleaching

Normal bleaching conditions Sequence	C/EH/D/	C/EH/D/
Experiment Nos.	6	7
Temperature, °C	60	68
Chlorine dioxide as such added, %	1.56	1.56
Chlorine dioxide as such consumed, %	1.26	1.52
Initial pH	7.0	7.0
Final pH	6.0	6.0
Retention time, mts.	230	100
Brightness, %	83	83
Viscosity, cP	58.5	54.5

From the above (Table No. IV) it is clear that the increase in temperature enhanced the rate of reactions. Almost all chlorine dioxide was consumed in 100 minutes at 68°C.

iii Strength properties: — For this, the pulps were obtained by bleaching the partly bleached pulp C/EH/ by different sequences using hypochlorite and chlorine dioxide. These pulps were beaten in a Lampen Ball Mill to 40°SR and standard sheets on British Sheet Making Machine were made. The sheets were tested for strength after conditioning. For comparison the strength of foreign "PUGET" pulp used at that time in mill are given.

The bleaching conditions and strength properties are recorded in Table No. V and VI respectively.

TABLE V
Bleaching conditions and results

Normal bleaching conditions Experiment Nos. Sequence	8 C/EH/	9 C/EH/H/	10 C/EH/D/	11 C/EH/D/
1. Hypo stage Hypo consumed, %	—	1.2	—	1.2
2. Chlorine dioxide stage Chlorine dioxide as such added, %	—	—	1.0	0.6
Chlorine dioxide as such consumed, %	—	—	1.0	0.6
Initial pH	—	—	4.0	6.0
Final pH	—	—	3.0	4.5
Brightness, %	69	80	83.5	85.0
Viscosity, cP	58.5	29.0	61.5	29.0

TABLE NO. VI
Strength properties

Experiment Nos. Sequence	8 C/EH/	9 C/EH/H/	10 C/EH/D/	11 C/EH/H/D/	12 "Puget" pulp
Brightness, %	69	80	83.5	85	84
Viscosity, cP	58.5	29	61.5	29	—
Basis wt. g/m²	61.3	56.5	58.2	57.8	59.8
Bulk, cc/g.	1.50	1.55	1.51	1.49	1.59
Breaking length, m.	6040	5310	6360	5390	6400
Stretch, %	4.5	3.5	4.1	3.6	4.6
Tear factor	81.6	64.5	87	63.4	108.6
Burst factor	42.6	28.8	44.7	33.0	50.2

The use of hypochlorite after the C/EH/stage considerably degraded the pulp as indicated by the drop in viscosity and strength properties.

The use of about one per cent Chlorine dioxide after the C/EH/stage (Expt. 10) increased the brightness to 83.5% and strength properties of this pulp were comparable to the strength of imported 'PUGET' pulp (Expt. 12).

iv As it was not possible to get higher brightness in 3 and 4 bleaching stages, the number of stages were increased in the following study. The basic sequence was C/EH/. In all the cases about 1.0% calcium hypochlorite was applied after C/EH/stage to get about 78% brightness. Afterwards the chlorine dioxide was applied. In one sequence the final treatment was of hypochlorite. A very small amount of hypo (0.2%) was applied. The bleaching sequences were from 5 to 7. The results are given in Table No. VII.

Pulp brightness obtained was about 86% in six stages and 87% in seven stages where the introduction of extra caustic extraction after hypo increased the brightness by one point. The chlorine dioxide consumed as such was about 0.8—1.1 per cent. The introduction of hypo stage after D1 stage considerably degraded the pulp as indicated by viscosity drop (Expt. No. 15) The maximum brightness that was achieved in this study was 87 per cent.

v After C/E/stage the hypochlorite was applied to get about 77—78% brightness. A series of bleaching sequences were studied to get high brightness. The number of stages were 5 and 6. At the end of bleaching the sulphur dioxide treatment was given in each sequence for about 15 minutes at 4.5—5.0 pH.

The results are recorded in Table No. VIII.

The chlorine dioxide was applied after the conventional C/E/H/sequence. In Expt. No. 16 after C/E/H/ stage there was caustic extraction and pulp brightness achieved was 86% with a single chlorine dioxide stage consuming one per cent of chlorine dioxide. In the Expt. No. 17 hypochlorite addition after chlorine dioxide was not found useful. The C/E/H/D1/E/D2/sequence (Expt. No. 18) appeared to be practicable in view of its low bleach consumption and achieving 88% brightness. Since this sequence was applied to a hard pulp (K. No. 28.3) it could not be compared to other two sequences (Expt. 16 and 17).

vi The K. No. of unbleached pulps used in this study was 28.3. The high K. Numbers were maintained to get higher pulp yield and good strength. In such cases, where residual lignin is high double chlorination with intermediate alkali stage is recommended (14,15) to minimise the cost of bleaching and the degradation of cellulose. Therefore the $C_1/E/C_{a_1}/E$/stage was tried. In this study in one sequence no hypochlorite was applied. At the end SO_2 treatment was given in each case as earlier. The $C/E_1/C/E_2/D_1/E_3/D_2$ and $C_2/E_1/C/E_3/H/D$ sequences were studied and the results are recorded in Table No. IX.

In this study it was possible to apply effectively the chlorine dioxide after reducing the lignin content considerably by double chlorination. Without the use of hypochlorite the brightness achieved was 87%, by two chlorine dioxide stages. However, the chlorine dioxide consumption was about 1.4 per cent.

The sequence $C_1/E_1/C_2/E_2/H/D/$ (Expt. No. 20) appeared better than the $C_1/E_1/C_2/E_2/D_1/E_3/D_2/$ (Expt. No. 19) sequence where the brightness obtained were nearly the same but there was 1.0% less chlorine dioxide consumption.

TABLE NO. VII

Study of C/EH/H/D1/E/$D2, C/EH/H/D1/H/sequences	C/EH/H/E1/D1/E2/D2/ and C/EH/H.....		
Normal bleaching conditions			
Permanganate number of unbleached pulp		22.6	
Experiments Nos.	13	14	15
Sequence	D1/EI/D2/	E1/D1/E2/D2	D1/H_3
1. Alkali extraction, E_1			
Caustic soda added, %	—	1.0	—
2. Chlorine dioxide, D_1			
Chlorine dioxide added as such, %	0.54	0.58	0.80
Chlorine dioxide consumed as such, %	0.51	0.54	0.66
Time, mts.	150	150	150
3. Hypo stage, H_3			
Hypo added as chlorine, %	—	—	0.20
Hypo consumed as chlorine, %	—	—	0.16
Time, mts	—	—	60
Brightness, %	—	—	84
4. Alkali stage, E_2			
Caustic soda added, %	1.0	1.0	—
5. Chlorine dioxide, D_2			
Chlorine dioxide added as such, %	0.65	0.40	—
Chlorine dioxide consumed as such, %	0.60	0.31	—
Time, mts.	180	180	—
Brightness, %	86	87	—
No. of stages	6	7	5
Chlorine consumed, %	9	9	9
Hypochlorite consumed, %	5.5	5.5	5.7
Caustic soda consumed, %	3.0	4.0	2.0
Chlorine dioxide consumed as such, %	1.1	0.85	0.65
Brightness, %	86	87	84
Viscosity, cP	More than 80	More than 80	55

TABLE VIII
Study of C/E/H/.....sequence

Normal bleaching conditions			
Permanganate Nos.	22.5	22.5	28.3
Experiment Nos.	16	17	18
Sequence	C/E/H/E2/ D1/	C/E/H1/ D1/H2	C/E1/H/ D1/E2/D2/
1. Chlorination, C			
Chlorine added, %	6.7	6.7	11.2
Chlorine consumed, %	6.5	6.5	11.0
Chlorine consumed, %			
2. Alkali extraction, E			
Caustic soda added, %	2.0	2.0	2.5
3. Hypo stage, H			
Hypo added, %	3.1	3.1	3.0
	3.0	3.0	2.64
Time, mts.	120	120	90
Brightness, %	78	78	78
4. Alkali extraction, E_2			
Caustic soda added, %	1.0	—	1.0
5. Chlorine dioxide, D_1			
Chlorine dioxide added as such, %	1.08	0.71	0.80
Chlorine dioxide consumed as such, %	1.0	0.68	0.80
Time, mts.	150	120	—
Brightness, %	86	—	—
6. Chlorine dioxide, D_2			
Chlorine dioxide added as such, %	—	—	0.46
Chlorine dioxide consumed as such, %	—	—	0.40
7. Hypo stage, H_2			
Hypo added, %	—	0.30	—
Hypo consumed, %	—	0.22	—
Brightness, %	—	85	—
Number stages	5	5	6
Chlorine consumed, %	6.5	6.5	11.0
Hypo consumed, %	3.0	3.22	2.64
Hypo consumed, %	3.0	2.0	2.64
Caustic soda consumed, %	3.0	2.0	3.5
Chlorine dioxide, %	1.0	0.7	1.16
Brightness, %	86	85	88
Viscosity, cP	—	49.3	30.5

PART II

i Optimum ratio of chlorine to chlorine dioxide:

For the better delignification and overall improvement in quality of pulp, the chlorine dioxide was used along with chlorine for the bamboo sulphate pulp. A set of experiments were carried out to find out an optimum ratio of chlorine to chlorine dioxide in the first stage for the bamboo pulp. The chlorine dioxide was substituted for an equivalent amount of chlorine (1.g. chlorine dioxide = 2.63 g chlorine) in a series of experiments covering from all chlorine to all chlorine dioxide. The chlorine demand in the first stage was 10.0%. This was determinded as suggested by Baldauf and Lehto (16) The application of the mixture of chlorine and chlorine dioxide was carried out at normal bleaching conditions. Then the washed pulps were extracted with 2.5% caustic soda for one hour at 50°C temperature. The results of the extracted pulps are given in Table No. X.

It is seen from Table No. X that the optimum ratio of chlorine to chlorine dioxide was 25 to 75. At this ratio the removal of lignin and the brightness of caustic extracted pulp was higher than in other cases (Fig. No. 1). The removal of inorganic constituents in pulp increased with increase of chlorine dioxide in the mixture as indicated by the lowering of ash content in the pulp.

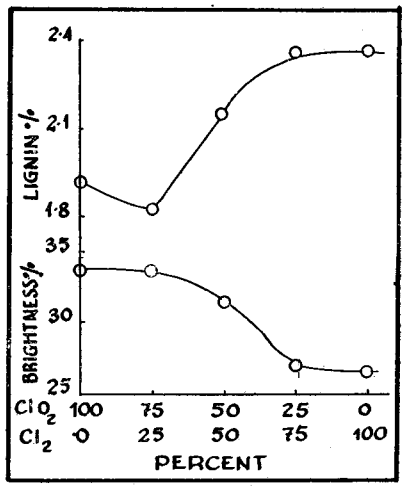

Fig. 1 : The Lignin content and brightness of pulp at different ratios of chlorine to chlorine dioxide.

ii Study of different bleaching sequences:

Using the optimum ratio of chlorin e : chlorine dioxide 25 : 75 in the first stage, two bleaching sequences were studied to get high pulp brightness and strength. The bleaching sequences studied were CD/E/H/D_1/E_2/D_3/ and CD/E_1/C/E_2/H/D/. The results are given in the Table No. XI.

The brightness obtained in the sequences CD/E_1/H/D_1/E_2/D_2/ and CD/E/C/E_2/H/D were 88.0% and 87.0% respectively with same viscosity. Here, the CD/E/C/EH/D/sequence appeared to be cheaper as there was only one stage of chlorine dioxide whereas in the sequence CD/E/H/D_1/E/D_2/ two stages were of chlorine dioxide. In this study the maximum brightness obtaintained was 88.0% with six bleaching stages for the pulp studied. The chlorine dioxide consumption was quite high (3.6—4.7 per cent) which increases the cost of bleached pulp.

iii Ceiling point of brightness

The study made so far in part I and II revealed that the brightness of pulp could not be raised beyond 89% in six or seven stages. It is reported that each type of pulp has got a particular ceiling point of brightness beyond which the increase in

TABLE IX

Study of sequences C/E1/C/E2/D1/E3/D2 and C/E/C/E/H/D/

Normal bleaching conditions		
Permanganate No.	28.3	
Experiment Nos.	19	20
Sequence	C/E1/C/E2/D1/ E3/D2	$C_1/E_1/C_3/E_2/H/D$
1. Chlorination, C_1		
Chlorine added, %	11.25	11.25
Chlorine consumed, %	11.00	11.00
2. Alkali extraction, E_1		
Caustic soda added, %	2.50	2.50
3. Colorination, C_2		
Chlorine added, %	3.00	2.20
Chlorine consumed, %	2.70	2.00
Time, mts.	40	40
4. Alkali extraction, E_2		
Caustic soda added, %	1.0	1.5
Time, mts.	45	45
5. Hypo stage, H		
Hypo added, %	—	1.0
Hypo consumed, %	—	0.82
Time, mts.	—	80
Brightness, %	—	81.0
6. Chlorine dioxide, D_1		
Chlorine dioxide added as such, %	0.80	0.50
Chlorine dioxide consumed, as such, %	0.79	0.44
Time, mts.	80	150
Brightness, %	—	86
7. Alkali extraction, E_3		
Caustic soda added, %	1.0	—
Time, mts.	40	—
8. Chlorine dioxide, D_2		
Chlorine dioxide added as such, %	0.80	—
Chlorine dioxide consumed as such, %	0.68	—
Time, mts.	180	—
Brightnes, %	87	—
Number of stages	7	6
Brightness, %	87	86
Viscosity, cP	51	—
Hypo consumed, %	—	0.82
Chlorine dioxide consumed as such, %	1.47	0.44

TABLE NO. X

Study of optimum ratio of chlorine to chlorine dioxide

Permanganate No.	28.3				
Experiment Nos.	21	22	23	24	25
Sequence	D/E	CD/E	CD/E	CD/E	C/E
Chlorine dioxide, %	100	75	50	25	0
Chlorine, %	0	25	50	75	100
Permanganate No.	8.6	8.4	9.3	10.7	10.6
Lignin, %	1.92	1.83	2.16	2.37	2.37
Ash; %	0.15	0.17	0.18	0.33	0.29
Brightness, %	34.0	34.0	31.5	27.0	26.5

bleaching stages does not improve the brightness. So a study was made to find not the ceiling point of brightness for the bamboo sulphate pulp having K. No. 28.3.

In the first stage chlorine and chlorine dioxide mixture was used as in Part II. The caustic extraction was carried out at 50°C for one hour with 2.5% NaOH. After washing, calcium hypochlorite was applied. The total number of stages were eleven. This study was carried out for an academic interest. The bleaching conditions and results are recorded in Table No. XII.

A graph (Fig. 2) showing the trend in increase of brightness against the number of bleaching stage was plotted.

The brightness could not be raised beyond 89% even by increasing the bleaching stages. In six stages, it was possible to get 88% brightness. Afterwards in the 8th stage the brightness was increased by a single point afterwards it remained constant. For the pulp studied, the ceiling point of brightness was 89.0 per cent.

PART III Sequential use of chlorine dioxide and chlorine in first bleaching stage Dc/:

Some experiments were done in laboratory on bamboo sulfate pulp employing sequential addition. The optimum chlorine demand of the pulp in the first stage was found to be 8.0%. Then 20% and 40% respectively of chlorine demand in the first stage were replaced by chlorine dioxide in terms of equivalent chlorine. The pulps were washed and caustic extractions were carried out and further bleached by hypochlorite to about 80% brightness. A control experiment was also carried out where chlorine dioxide was not applied. The results with bleaching conditions are recorded below in Table No. XIII.

The above results show that there is increase in brightness and viscosity and reduction of total chlorine consumption in the case where 40% of chlorine demand was replaced by chlorine dioxide in the first stage. But the improvement is not significant if the cost of chlorine dioxide is taken into consideration.

DISCUSSION

The Permanganate Number of pulps used in this study were in the range of 23-28. These are rather hard cooked pulps which would consume large amount of bleaching agents. For these pulps, the pulp yield ranges from 50-52 per cent on the basis of oven dry bamboo chips.

When the chlorine dioxide was applied after the C/E/stage it did not improve the brightness of pulp. This indicated that the chlorine dioxide is not useful if it is applied after the C/E/stage for the pulp studied when the lignin content in the partly bleached is high ($KMnO_4$ No. 10.5) (Table No. I).

TABLE NO XI
Study of sequences CD/E1/H/D1/E2/D2/ and CD/E1/C/E2/H/D

Normal bleaching conditions		
Permanangeant No.	28.3	
Experiment No.	26	27
Sequence	CD/E1/H/D1/ E2/D2	CD/E1/C/ E2/H/D
1. First stage, CD		
Ratio of chlorine to chlorine dioxide	25:75	25:75
Chlorine and Chlorine dioxide as chlorine, %	10.0	10.0
2. Caustic extraction, E1		
Caustic soda, %	2.5	2.5
3. Chlorination, C		
Chlorine used, %	2.5	2.5
4. Hypo stage, H		
Hypo used, %	3.0	—
Retention time, mts.	100	—
Brightness, %	77	
5. Chlorine dioxide stage, D1		
Chlorine dioxide consumed as such, %	1.08	—
Retention time, mts.	150	—
Brightness, %	83.5	—
5. Caustic extraction, E2		
Caustic soda applied, %	1.0	2.0
7. Hypo stage, H		
Hypo consumed, %	—	0.8
Brightness, %	—	81.0
8. Chlorine dioxide, D2		
Chlorine dioxide as such, %	0.70	0.80
Retention time, mts.	180	180
Elemental chlorine consumed, %	2.5	6.0
Hypo consumed, %	3.0	0.8
Chlorine dioxide consumed as such %	4.70	3.65
Caustic soda consumed, %	3.5	4.5
Brightness, %	88	87
Viscosity, cP	72.5	73.5

The C/EH/stage was carried out to get about 70 per cent pulp brightness. Then various sequences were studied. It was found that 83.5 per cent brightness could be obtained in three bleaching stages C/EH/D/consuming about 1.0 per cent chlorine dioxide (Table No. V). The strength of pulp obtained by this bleaching sequence compared favourably with the strength of imported 'PUGET' pulp (Table No. VI). However, the consumption of hypochlorite is high. This could be explained that during the EH stag the chlorolignins left in the pulp after chlorination that are normally removed during the alkali extraction consume bleach liquor for dissolving out of the pulp.

To avoid this excessive consumption of hypochlorite and to get good initial brightness the C/E/H/sequence was tried. The C/E/H/$D_1/E_2/D_2$/sequence gave 88 per cent brightness consuming 1.17 per cent chlorine dioxide.

The double chlorination of pulp with intermediate alkali extraction for pulps of permangnate number 28.3 was carried out to reduce the bleaching cost. The hypochlorite application after the $C_1/E_1/C_2/E_2$/ stage gave pulp of 81 per cent brightness (Table No. IX).

The application of 0.45 per cent chlorine dioxide after C_1/E/C/E/H/ stage (Table No. IX) gave 86 per cent brightness. This sequence appears to be economically viable for bleaching the bamboo sulphate pulp of high permanganate number.

The use of chlorine dioxide and chlorine mixture in this first stage was found to give higher brightness pulp and with lower permanganate number after caustic extraction compared to when chlorine alone was used (Table No. X). The optimum ratio of chlorine dioxide to chlorine was found to be 75:25 in the first stage (Table No. X). In this case a large amount of chlorine dioxide (about 3.0 per cent) was consumed in the first stage which makes the use of mixture of chlorine dioxide and chlorine prohibitive due to high cost of chlorine dioxide when compared to chlorine gas.

The ceiling point of the brightness for the pulps studied of KMnO4 No. 28.3 found to be 89 per cent (Table No. XII).

One of the most efficient method of lignin removal has been the sequential addition of chlorine dioxide. It was studied for the bamboo pulp of KMnO4 21.9. The 40 per cent chlorine demand in the first stage was replaced by chlorine dioxide in terms of chlorine. This gave an increase in viscosity of pulp and also reduced the total chlorine consumption (Table No. XIII). Further work is to be carried out to evaluate fully the benefits of the sequential addition for bamboo sulphate pulps of high permanganate numbers.

In India at present chlorine dioxide is manufactured by Matheison process where sulphur dioxide is used as a reducing agent. The R2 process by Rapson which has been patented under patent No. 2,863,722 issued to W. Ho ward Rapson and assigned to Hooker Chemical Corporation in the USA is the best method. The price break up (17) of the above is given in Table No. XIV.

It could be seen from Table XIV. that the price of chlorine dioxide by R2 process is significantly lower than that by Mathieson process. Taking the price of chemicals in India required for R2 process the chemical cost per Kg of chlorine dioxide is given in Table No. XV.

For a 100 tonne pulp plant, the chlorine dioxide required for bleaching by the two sequences C/E/H/D/E/D and C/E/C/E/H/D for pulps of permanganate numbers of 26-28 would be 1200 Kg and 460 Kg respectively. This will cost around Rs. 3,392 and Rs. 1,338 respectively for the sequences and would require a chlorine dioxide plant of one tonne per day capacity. It is believed that the resulting pulp obtained by the chlorine dioxide would be characterised by satisfactory yield, high brightness and high strength.

TABLE XII
Several stages of bleaching of high K.NO pulp

Normal bleaching conditions	
Permanganate No.	28.3
Expernment No.	28
1. First stage — Mixture of chlorine and chlorine dioxide 25:75	
Chlorine added, %	2.5
Chlorine dioxide added as such, %	3.0
Total chlorine and chlorine dioxide as chlorine, %	10.0
2. Caustic extraction, E1	
Caustic soda added, %	2.5
Time, mts.	60
3. Hypochlorite stage, H	
Hypo added, %	3.1
Hypo consumed, %	3.0
Brightness, %	78
4. Chlorine dioxide, D1	
Chlorine dioxide added as such, %	1.16
Chlorine dioxide consumed as such, %	1.08
Time, mts.	150
Brightness, %	85
5. Caustic extraction, E2	
Caustic soda added, %	1.0
Time, mts.	45
6. Chlorine dioxide, D2	
Chlorine dioxide added as such, %	0.80
Chlorine dioxide consumed as such, %	0.70
Time, mts.	180
Brightness, %	88
7. Caustic extraction, E3	
Caustic Soda added, %	1.0
Time, mts.	45
8. Chlorine dioxide, D3	
Chlorine dioxide added as such, %	0.80
Chlorine dioxide consumed as such, %	0.60
Time, mts.	180
Brightness, %	89
9. Caustic extraction, E4	
Caustic soda added, %	1.0
Time, mts.	45
10. Chlorine dioxide, D4	
Chlorine dioxide added as such, %	0.80
Chlorine dioxide consumed as such, %	0.60
Time, mts.	180
Brightness, %	89
11. Chlorine dioxide, D5	
Chlorine dioxide added as such, %	0.60
Chlorine dioxide consumed as such, %	0.40
Time, mts.	180
Brightness, %	89

TABLE No. XIII
Study of sequential addition DC/E/H sequence

KMnOC₄ No.		21.0	
Chlorine demand in the first stage,	%	8.0%	
Experiment Nos.	29	30	31
Sequence	C/E/H/	Dc/E/H/	Dc/E/H/
I 1st Stage:			
Chlorine dioxide treatment			
1. Part of chlorine replaced by chlorine dioxide in terms of chlorine, %	—	20	40
2. Consistency, %	—	5.0	5.0
3. Retention time, mts.	—	3	8
4. Chlorine treatment, chlorine applied %	100	80	60
5. Retention time, mts.	60	57	52
6. Total period in 1st stage, mts.	60	60	60
7. Chlorine consumption, %	7.4	7.3	7.3

CONCLUSION

1 The chlorine dioxide bleaching is the most effective agent for bleaching the bamboo sulphate pulp of high K.No. to high brightness pulp of satisfactory strength properties.

2 The chlorine dioxide is very effective if added at the end of the bleaching sequences where the brightness of pulp is over 70 per cent.

3 The seuence C/E/H/D/E/D/ and C/E/C/E/H/D/appeared to be the most effective for bamboo sulphate pulps of permanganate number 26-28.

4 A one tonne per day chlorine dioxide plant should be sufficient to meet the bleach demand of 100 tonnes unbleached pulp using the sequence C/E/H/D/E/D as well as C/E/C/E/H/D.

5 The chemical cost of chlorine dioxide in India should be about Rs. 2.91 per Kg that in terms of chlorine Rs. 1.2 per Kg. Considering the benefits of chlorine dioxide this should be feasible for bleaching bamboo pulp.

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II Caustic extraction, E.			
Caustic soda, %	2.0	2.0	2.0
III Hypochlorite stage, H			
Hypo added, %	3.0	2.5	2.0
Hypo consumed, %	2.4	2.1	1.56
Total Chlorine consumption, %	9.8	9.4	8.86
Brightness, %	75	76	77
Viscosity, cP	41.2	43.5	56.5

TABLE No. XIV

Chemical cost comparison of the two processes for the manufacture of chrorine dioxide.

	R2 Process lb. cents/lb. Cents	Mathieson Process lb. Cents/lb. Cents
Reactants		
Sodium chlorate	1.66 x 9.0=14.9	1.85 x 9.0=16.7
Sulphuric acid	4.75 x 1.1= 5.2	1.3 x 1.1= 1.4
Sodium chloride	0.9 x 0.7 =0.6	..
Sulphur dioxide	..	0.85 x 4.5=3.8
Gross chemical cost	20.7	21.4
Credits		
Sodium sulphate	2.3 x 1.7=3.9	1.2 x 1.7= 2.0
Chlorine	0.4 x 3.5=1.4	..
Sulphuric acid	3.2 x 1.1=3.5	1.7 x 1.1= 1.9
Total credits	8.8	3.9
Net chemical cost	11.9	17.5

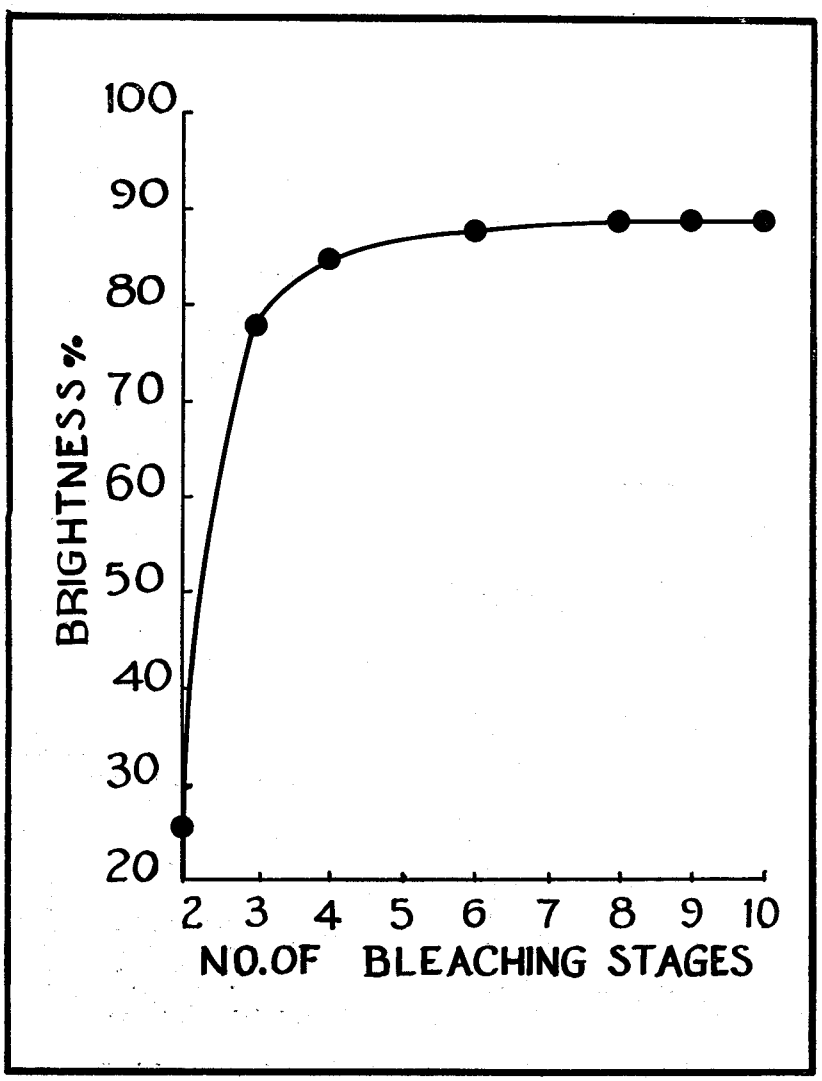

Fig. 2 : Brightness of pulp at different bleaching stages.

TABLE No. XV

Chemical cost per Kg chlorine dioxide by R2-process in India

	Kg	Rs/Kg	Rs.
Sodium chlorate	1.66	x 2.45	4.07
Sulphuric acid	4.75	x 0.4	1.90
Sodium Chloride	0.9	x 0.1	0.09
Gros chemical cost			6.06
Credits			
Sodium sulphate	2.3	x 0.75	1.73
Chlorine	0.4	x 0.35	0.14
Sulphuric acid	3.2	x 0.40	1.28
Total credits			3.15
Net chemical cost			2.91

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