Formaldehyde: A Useful Bleaching Aid To Save On Bleach Chemical Cost Sahoo Sarita, Tripathy D.K., Panigrahi J.C. & Harichandan A.K.

ABSTRACT

Presently pulp and paper industries use additives in pulping, oxygen delignification and bleaching to enhance the reactions and reducing the processing costs. Simple member of the family of aldehydes (formaldehyde) and ketones (acetone) having a carbonyl group (-C=O) are effective as additive to increase the efficiency of chlorine dioxide bleaching. The performance studies of these additives to bleach the pulp samples after ODL with our raw materials at two different furnishes (100% mixed hardwood and bamboo: MHW 20:80) have been carried out to a target brightness of $89\pm1\%$ ISO. The addition and effect of brightness gain was utilized for the reduction of high cost bleaching chemicals like H₂O₂ and ClO₂ in subsequent bleaching stages.

The paper describes how formaldehyde can be useful in saving 10.4~kg/ton of $50\%~H_2O_2$ solution or 2.66~kg/ton of ClO_2 in a bleaching sequence of CD-Ep-D. In the process, the resultant pulp quality was also found to be better with respect to brightness, viscosity and strength properties. A decrease in pitch content was observed alongwith a reduction of TSS in the combined effluent. An indication of cost aspect has also been covered in this paper. Acetone did not prove useful inspite of saving 12~kg/ton of H_2O_2 (50% solution) and 4.18~kg/ton of ClO_2 due to its high cost.

Introduction

Formaldehyde, a simple organic solvent has a carbonyl group (-C=O) which reacts with chlorites to release ClO₂ (1-3). In practice, industrial process wastes much of the ClO, by forming chlorite (ClO₂) and chlorate (ClO₃). Chlorite is normally formed in the chlorination stage by both ionic and free radical mechanisms. Chlorine dioxide ionises to chlorate (ClO₃), chlorite (ClO₂) and chloride (Cl) where hypochlorous acid (HClO) and chlorous acid (HClO₂) are produced as reaction intermediates depending on pH (4, 5). Chlorite is also formed by reduction of ClO₂ on reaction with phenolic groups in lignin to give phenoxy radicals by one electron oxidation.

Realising the high cost of ClO₂ generation, it was aimed at converting the ClO₂ or HClO₂ formed in situ, to ClO₂, by use of two organic chemicals, i.e. formaldehyde and acetone. Both of these chemicals were oxidized to their respective carboxylic acid on reaction with HClO₂ and liberated ClO₂ as the byproduct. This conversion of inactive chlorite or chlorous acid to ClO₂, increases the bleaching efficiency thereby resulting in increased brightness of final bleached pulp. The

Pulp and Paper Research Institute, Jaykaypur 765 017, Dist. Rayagada (ORISSA). increased brightness and bleaching efficiency of ClO₂ can translate into bleach chemical saving in further stages of bleaching.

A mill trial of aldehyde enhanced bleaching for 3 days in 2001 in a Canadian mill was also reported (3), wherein a saving of 10.8 kg. of ClO₂ per ton of pulp at a target brightness of 89.2% was achieved. Therefore a study was undertaken to see the possibility of arresting the chlorite formation or conversely to regenerate ClO₂ from chlorites so that bleaching efficiency and utilization of bleach chemicals are optimized.

Although acetone was found to be equally effective compared to formaldehyde but due to its high cost (Rs.72/kg.) and hazardous nature, the study was pursued with formaldehyde for a possible industrial application.

Understanding the mechanism:

The study was carried out in a bleaching sequence of CD-Ep-D. In CD stage of pulp bleaching, both Cl₂ and ClO₂ are added to pulp simultaneously, first chlorine followed by ClO₂. Initially, molecular chlorine and hypochlorous acid (HOCl) are in equilibrium with equal quantities present at pH 2 and 25°C (6). When ClO₂ is added to pulp, it reacts with pulp transferring one electron to produce chlorite ion (ClO₂). This chlorite is unreactive towards lignin, Under acidic pH conditions, it is

converted to HClO₂ which oxidizes lignin, to form HClO. The formation of chlorite or chlorous acid represents a loss of oxidizing efficiency of ClO₂(7). A most plausible mechanism of various parallel reactions involving HOCl, ClO₂, clO₂, aldehydes and the pulp in the CD stage is discussed below:

It is generally accepted that both ionic and free radical mechanisms are involved in chlorination of pulp. Ionic reactions are predominant with lignin and radical reactions with carbohydrates. Lignin acts as an effective radical scavenger by virtue of favourable reaction kinetics and protected carbohydrates from oxidation. This protective effect diminishes when lignin content Chlorine dioxide is decreases. therefore added to pulp to protect radical attack in the CD stage (6). Literature reveals that within few minutes after the chlorination stage, 32% of ClO₂ is converted to active chlorite resulting in loss of oxidizing power (8). Addition of formaldehyde prevents the loss of oxidation potential of ClO₂ by generating ClO₂ from The carbonyl group in formaldehyde converts the chlorous acid (HClO₂) and chlorite (ClO₂), formed in situ to give back the ClO₂(9). In CD stage, where chlorination is carried out at or below pH-2, one of the ionisation products of ClO₂ i.e. chlorite ClO₂ is maximum. Chlorite is also regenerated by the reduction of ClO₂ on reaction with the phenolic groups of residual lignin to give phenoxy radicals by one electron oxidation (8). This can be represented in the equation below: Phenol + 2 ClO₂ → Products + ClO₂ + HOCl (p-quinones or hydrogen methyl muconates)

At this strongly acidic pH condition, chlorite (ClO₂) is found to be in equilibrium with chlorous acid as per the equation:

$$ClO_{2}^{-}+H^{+}\rightarrow HClO_{2}$$
 -----(i)

Formaldehyde, if added at this stage, reduces the chlorite to ClO₂ and is itself oxidized to formic acid according to the following equation (10):

$$H-CHO + H^{+} + ClO_{2} \rightarrow HOC1 + HCOOH ----- (ii)$$

As the above reaction proceeds, pH of the solution drops due to formation of formic acid. The increased acidity of the solution promotes the formation of CIO, as shown below:

In acidic solution, ClO₂ behaves as an oxidizing agent. The complete reduction of ClO₂ is shown below:

$$ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O$$
----(iv)

The individual steps of reaction (iv) produces HClO₂, HOCl and Cl₂ and all behave as oxidizing agents.

The overall reactions of chlorite during chlorination (CD stage) after formaldehyde addition can be represented as below (11):

$$\Phi HOCl + 2HClO_2 \rightarrow 2ClO_2 + H2O + H^+
+ Cl$$

$$H-CHO+3HC1O_2 \rightarrow H-COOH+2C1O_2+H_2O+HC1$$

At higher pH levels above 4 chlorate formation increases when hypochlorous acid reacts with chlorite which also represents loss of oxidizing power of ClO₂ (12).

 $HClO + ClO_2 \longrightarrow ClO_3 + H^+ + Cl^-$

EXPERIMENTAL

Preliminary Study

The experiments were carried out using two types of pulp samples i.e. i) a mixture of hardwood, ii) a mixture of bamboo and hardwood [20 : 80] after oxygen delignification at PAPRI. They were bleached in a CD-Ep-D sequence and before bleaching the kappa no., brightness and consistency were checked.

Preliminary experiments were conducted with 100 gm. of OD pulp (in small polythene bags) following above sequence to know the maximum effectiveness of formaldehyde and the mode of addition to pulp. Experiments were also carried out by adding formaldehyde to the D-stage in addition to the CD stage. The optimum dose of formaldehyde on pulp was added at CD stage followed by Ep stage. The Ep pulp was split in two parts; to the first part formaldehyde was added with ClO₂ in D stage and to the other only ClO₂ was added (blank).

Optimization of Formaldehyde and Acetone Dosing

Three levels of formaldehyde dose i.e. 0.25%, 0.75% and 1.0% and acetone dose of 0.75%, 1.0% and 1.5% on O.D. basis of pulp were tried for optimization.

Detailed Study

Four sets of pulp samples from the mixed hardwood furnish were chosen for detailed study with 400 gm. O.D. pulp. Later on, the similar sets were repeated with B + HW furnish. The first set was taken as blank, second set was with the optimum dose of formaldehyde, third and fourth sets were with reduced dose of peroxide and chlorine dioxide respectively maintaining same dose of formaldehyde. The resultant bleached pulp was evaluated for brightness, viscosity, fibre fractions and strength properties at 40 °SR beaten pulp. Stage wise process conditions and other pulp properties are tabulated in Table 1.

- ◆ Set I: Blank (without Formaldehyde addition): A control or blank experiment was done without using formaldehyde using lab scale bleaching conditions standardized at Pulp and Paper Research Institute in CD-Ep-D sequence. Basis of total chlorine demand was calculated as 52% of ODL kappa no. 70% of this given at CD stage and 30% at D stage.
- Set II: Addition of 0.75% Formaldehyde: To the second set

of pulp, 0.75% formaldehyde was added in the CD stage by mixing with chlorine dioxide. All other bleaching conditions were same as that of blank

- ◆ Set III: Addition of 0.75% of Formaldehyde and Reducing 35% of Peroxide Dose in EP Stage: To the third set of pulp, similarly formaldehyde was mixed in chlorine dioxide and added to pulp in CD stage and H₂O₂ dose in Ep stage was reduced from 1.5% to 0.98%.
- ◆ Set IV: Addition of 0.75% of Formaldehyde and Reducing 30% of CIO2 Dose in D Stage:

 To the fourth set similarly 0.75% formaldehyde was added to CIO₂ at CD stage but here the CIO₂ dose in D stage was reduced by 30% as compared to blank.
- ♦ The total suspended solids (TSS) of the combined effluent mixed in the ratio of CD: Ep: D at 2:1:3 was checked taking 1 litre. of effluent and filtering it through the normal filter paper. The initial and final weight of the filter paper was taken to calculate the TSS which gives an indirect indication of fines content.
- ◆ To know the pitch content in the final D stage pulp, the standard procedure for DCM (Dichloromethane) extraction using a soxhlet apparatus was followed (Tappi Test Methods: T-204).

All the final stage bleached pulps were evaluated for brightness, viscosity, fibre fractions, strength properties, TSS and DCM extractives. Set I - IV experiments were conducted with 100% hardwood (HW) furnish. All process conditions and pulp properties are given in Table-1.

A repeat set of experiments were conducted taking B + HW (20 : 80), process conditions and test parameters remained unchanged (Set I-A to IV-A). Results are presented in Table-2.

Similar experiments were done as above with acetone at an optimized dose taking both HW and B + HW furnish. The results of these experiments are presented in Tables 3 and 4, process parameters and experimental conditions remaining same except the reducing doses of H₂O₂ and ClO₃ (i. Blank without acetone, ii.

With 1% acetone, iii. With 1% acetone +40% less H_2O_2 , iv. 1% acetone +60% less ClO_2 and v. 1% acetone +40% less $H_2O_2 + 50\%$ less ClO_3).

RESULTS AND DISCUSSION

A higher brightness (90.7% ISO) was obtained when formaldehyde was mixed with ClO₂ and added to pulp than that by adding directly to pulp (88.9% ISO) and without formaldehyde i.e. blank (87.8% ISO). Hence, adding formaldehyde to ClO₂ was more effective than adding it directly to the pulp.

The dose of formaldehyde at 0.75% on O.D. pulp basis was found to be the optimum (with respect to brightness and viscosity) and detailed experiments on 400 gm. scale were carried out, at this dosing. Optimization of formaldehyde dose with respect to brightness has been indicated in Figure-1. Similarly, optimization of acetone by applying 0.75, 1.0 and 1.5% on O.D. pulp was done and the optimum dose of 1.0% on O.D. pulp was selected.

It was found that addition of formaldehyde in both CD and D stages reduced the brightness by 0.6% ISO i.e. 88.9% ISO compared to blank (89.5% ISO). After the formaldehyde dose was optimized in preliminary study, a detailed study (with 400 gm. of OD pulp) was carried out to optimize the dose of formaldehyde at the target brightness level of $89\pm1\%$ ISO.

WITH FORMALDEHYDE:

The results of study on 400 gm. scale showed that with the optimized 0.75% dose of formaldehyde on O.D. pulp basis, the yield, brightness, viscosity and strength properties increased when added to both 100% HW and B + HW furnish. A decrease in the amount of fines fraction and DCM extractive content in the final bleached pulp was also observed (Table 1 and 2).

The brightness increased from 88.1% ISO to 89.4% ISO in 100% HW furnish and 88.5% ISO to 90.6% ISO in B + HW furnish. The viscosity increase was 13.4% with formaldehyde addition as compared to blank in HW pulp whereas it was 1.3% in case of B + HW pulp. The strength index went up from 1508 to 1663 in 100% HW furnish(Table 1) whereas in case of B + HW, the rise was 1716 to 1797(Table 2). Yield increase was 0.2% in B + HW furnish but no increase was observed in HW furnish. The pitch or DCM extractive content was 42.4% less in

FIGURE 1: EFFECT OF FORMALDEHYDE DOSE ON FINAL BRIGHTNESS

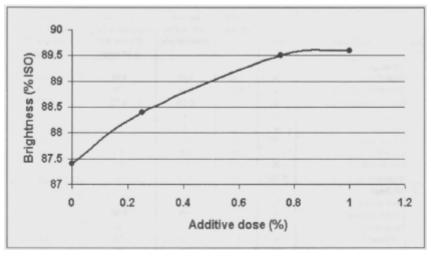


TABLE - 1: STUDY WITH FORMALDEHYDE (100% HW FURNISH)

PO Pulp unbleached kappa no.: 14.1

SI. No.	Particulars	Unit	Set-I (Blank)	Set-II (With 0.75% formaldehyde)	Set-III (Formald. 0.75% + 35% less H ₂ O ₂	Set-IV (Formald. 0.75% + (30% less CIO ₂
<u> </u>					in EP stage)	in D stage)
1	CD Stage Dose of Cl ₂	%	4.45	4.45	4.45	4.45
	Dose of CIO ₂ as CIO ₂	%	0.25	0.25	0.25	0.25
	Dose of Formaldehyde	%	U.23 -	0.25	0.25	0.75
	Consistency	%	8	0.73 8	8	8
	Retention	hr.	1	1	o 1	1
	Temperature	°C	r RT	RT	RT	RT
	End pH	0	1.8	2.1	1.5	1.9
	Residual Cl ₂	%	0.2	0.05	0.09	0.08
	Brightness	% ISO	52.3	54.3	54.8	54.1
2	EP Stage	70 100	52.5	54.5	34.0	34.1
	Alkali applied	%	2	2	2	2
	Dose of peroxide	%	1.5	1.5	0.98	1.5
	Consistency	%	10	10	10	10
	Retention	hr.	1.5	1.5	1.5	1.5
	Temperature	°C	80	80	80	80
	End pH	-	10.7	10.4	10.7	10.3
	Brightness	% ISO	76.6	77.8	75.4	78.1
3	D Stage	70.00				
	CIO ₂ applied as Cl ₂	%	2.2	2.2	2.2	1.5
	CIO ₂ consumed as CI ₂	%	1.9	1.96	1.75	1.36
	Consistency	%	10	10	10	10
	Retention	hr.	4	4	4	4
	Temperature	0C	70	70	70	70
	End pH	-	2.7	2.6	2.7	2.8
	Residual Cl ₂	%	0.3	0.24	0.45	0.14
	Brightness	% ISO	88.1	89.4	88.0	88.2
	Viscosity	cР	8.9	10.1	10.3	10.4
	Yield	%	93.0	93.0	92.7	93.4
	Shrinkage	%	7.0	7.1	7.3	6.6
4	Fibre classification :					
	+ 16	%	0.1	0.1	0.1	0.3
	- 16, + 30	%	0.2	0.7	0.2	0.2
	- 30, + 50	%	34.7	36.3	33.2	32.7
	- 50, + 100	%	32.0	31.0	33.2	33.9
	- 100	%	33.0	31.9	33.3	32.9
5	Beating time to get 40 ⁰ SR	min.	41	42	50	46
6	Strength properties :	2				
	Grammage	g/m ²	61.9	62.1	61.9	59.7
	Thickness	micron	94.5	93.3	86.9	87.2
	Bulk	cc/g	1.53	1.5	1.4	1.46
	Burst factor	-	39.9	41.4	46.4	45.6
1	Tear factor	-	65	76	71	67
1	Breaking length	mtr.	5924	5990	6688	6723
1	Double fold	no.	21	29	38	29
<u> </u>	Strength index		1508	1663	1733	1647
7	DCM extractive (pitch conter	ıt) %	0.33	0.19	-	-
8	TSS of combined effluent	ppm	1318	480	398	354
L	(CD:EP:D :: 2:1:3) ratio					

PO Pulp unbleached kappa no.: 14.1

			Set-I(A)	Set-II(A)	Set-III(A)	Set-IV(A)
SI.			(Blank)	(With 0.75%	(Formald. 0.75% +	(Formald. 0.75% +
No.	Particulars	Unit		formaldehyde)	35% less H ₂ O ₂	(30% less CIO ₂
					in EP stage)	in D stage)
1	CD Stage					
	Dose of Cl ₂	%	4.45	4.45	4.45	4.45
	Dose of CIO ₂ as CIO ₂	%	0.25	0.25	0.25	0.25
	Dose of Formaldehyde	%	-	0.75	0.75	0.75
	Consistency	%	8	8	8	8
	Retention	hr.	1	1	1	1
	Temperature	°C	RT	RT	RT	RT
	End pH	-	2.0	1.9	1.5	1.5
	Residual Cl ₂	%	0.21	0.5	0.2	0.2
	Brightness	% ISO	55.2	55.5	52.7	53.4
2	EP Stage					
	Alkali applied	%	2	2	2	2
	Dose of peroxide	%	1.5	1.5	0.98	1.5
	Consistency	%	10	10	10	10
	Retention	hr.	1.5	1.5	1.5	1.5
l	Temperature	°C	80	80	80	80
	End pH	-	10.7	10.6	10.9	10.6
	Brightness	% ISO	77.1	79.6	75.8	77.9
3	D Stage					
	CIO ₂ applied as CI ₂	%	2.2	2.2	2.2	1.5
	CIO ₂ consumed as CI ₂	%	1.7	1.8	1.9	1.4
	Consistency	%	10	10	10	10
	Retention	hr.	4	4	4	4
	Temperature	°C	70	70	70	70
	End pH	-	2.9	2.9	2.5	2.9
	Residual Cl ₂	%	0.5	0.4	0.30	0.13
	Brightness	% ISO	88.5	90.6	88.4	88.7
	Viscosity	cР	7.7	7.8	9.8	9.0
	Yield	%	94.6	94.8	94.7	94.9
	Shrinkage	%	5.4	5.2	5.3	5.1
4	Total Cl ₂ applied as Cl ₂	%	7.3	7.3	7.3	6.6
	Total Cl ₂ consumed as Cl ₂	%	6.6	6.4	6.8	6.3
5	Fibre classification :					
	+ 16	%	0.2	1.1	0.2	1.2
	- 16, + 30	%	8.5	5.4	10.1	8.3
	- 30, + 50	%	35.8	28.9	32.3	30.3
	- 50, + 100	%	24.8	23.5	24.2	24.5
	- 100	%	30.7	31.1	33.2	35.7
6	Beating time to get 40 ⁰ SR	min.	40	39	37	41
7	Strength properties :					
	Grammage	g/m ²	58.3	60.7	61.4	61.0
	Thickness	micron	88.4	91.8	89.1	86.2
l	Bulk	cc/g	1.51	1.51	1.45	1.41
l	Burst factor	-	48	49	52	51
l	Tear factor	-	72	73	75	75
l	Breaking length	mtr.	6323	6326	7166	6336
	Double fold	no.	29	42	57	39
1	Strength index	- %	1716 0.45	1797	1899	1826
۰			U.40	0.25	-	
8	DCM extractive (pitch content) TSS of combined effluent	ppm	1385	491	409	364

TABLE - 3: EFFECT OF ADDITION OF ACETONE IN HW FURNISH

	Brightness	Viscosity	Yield	Strength Properties				
Particulars	(% ISO)	(cP)	(%)	BF	TF	BL (mtr.)	DF (no.)	Strength Index
Blank	88.1	8.9	93.0	39.9	65	5924	21	1508
Acetone (1%)	89.4	9.5	93.8	40.5	63	5965	33	1571
Acetone + 40% less H ₂ O ₂	88.1	11.6	95.0	49.3	71	7029	63	1847
Acetone + 60% less ClO ₂	88.4	10.1	94.2	49.1	69	6873	40	1757
Acetone + 50% less ClO ₂ + 40% less H ₂ O ₂	88.4	12.3	95.8	53.4	68	7605	74	1893

formaldehyde added pulp as compared to blank in 100% HW furnish and 44.4% in B+HW furnish. This may be due to removal of HexA from pulp in

acidic conditions by the degradation of HexA in presence of HCHO thereby improving the final brightness (2).

At a similar brightness level by the addition of formaldehyde to pulp with reduced H₂O₂ or ClO₂ doses in the Ep and D stages, the viscosity was further improved to 15.7%, 16.8% (for HW) and 27.3%, 16.9% (for B + HW) simultaneously increasing the strength properties. The breaking length values were also increased to 6688, 6723 from 5924 (blank for HW) and to 7166, 6336 from 6323 (blank for B + HW) at reduced doses of H₂O₂ and ClO₂. The TSS representing the fraction of fines decreased in the combined effluent in all the experiments with formaldehyde in both 100% HW and B + HW furnishes.

WITH ACETONE:

An increase in brightness was observed from 88.1 to 89.4% ISO and 87.9 to 89.8% ISO respectively for HW and B + HW furnishes (Table 3 and 4). The viscosity increase was only 6.7% for HW pulp where as a significant increase of 13.4% was obtained with B + HW furnish. The strength index went up from 1508 to 1571 in HW pulp and from 1716 to 1869 in B + HW pulp. The pitch or DCM extractive content of acetone added pulps of both the furnishes was 0.16% against the blank (0.31% for HW and 0.33% for B +HW). The TSS in the combined effluent decreased to 534, 506, 594 and 586 ppm respectively in acetone added pulps compared to blank (1318 ppm). Also, at similar brightness level, the viscosity and strength properties of final pulp were increased very much at reduced dose of H₂O₂, ClO₂ and H₂O₂ + ClO, in Ep and D stages.

Viscosity increase against blank (%):

Particulars	<u>HW</u>	B + HW
$ReducedH_2O_2$	30.3	13.4
${\rm ReducedClO_2}$	13.5	19.5
Reduced H ₂ O ₂ +Cl	O ₂ 30.2	28.0

The strength index increased from 1508 (blank for HW) to 1847, 1757, 1893 and from 1716 (blank for B + HW) to 1919, 1822, 1844 respectively at reduced dose of H_2O_2 , ClO_2 and H_2O_2 + ClO_3 respectively.

COSTIMPACT:

Efforts were made to compare the differences in the cost of bleaching by use of formaldehyde for each set of experiments due to saving H_2O_2 and also ClO_2 . The values are given in Table 5 and 6.

TABLE – 4: EFFECT OF ADDITION OF ACETONE IN B +HW
FURNISH

	Brightness	Viscosity	Yield	Strength Properties				
Particulars	(% ISO)	(cP)	(%)	BF	TF	BL	DF	Strength
						(mtr.)	(no.)	Index
Blank	87.9	8.2	92.4	48	72	6323	29	1716
Acetone (1%)	89.8	9.3	93.7	49	72	6568	71	1869
Acetone + 40%	88.4	9.8	93.9	47	83	6789	65	1919
less H ₂ O ₂								
Acetone + 50%	88.5	9.1	93.8	50	76	6744	39	1822
less ClO ₂								
Acetone + 50%	88.3	10.5	93.4	49	83	6563	37	1854
less ClO ₂ + 40%								
less H ₂ O ₂								

Addition of 7.5 kg/ton of 40% formaldehyde solution at CD stage, it is possible to save about 2.66 kg/ton of ClO_2 or 10.4 kg/ton of H_2O_2 (50% solution) at Ep stage. The cost benefit analysis shows that with formaldehyde, a net savings to the tune of Rs. 63.80/ton of B.D. pulp can be made by reducing the H_2O_2 dose. While the net savings in cost is Rs. 21.20 / per ton of B.D. pulp was obtained in saving ClO_2 .

The cost of acetone at a dose of 10 kg/ton of B.D. pulp is comparatively high (approximately Rs. 720/-) compared to the costs towards combined savings of 12 kg/ton of $\rm H_2O_2$ (50% solution) and 4.18 kg/ton of $\rm ClO_2$ (Rs. 264+292.60=Rs. 556.60/-/ton).

CONCLUSION

Formaldehyde can be utilized as a possible bleaching aid to achieve optimum efficiency of ClO₂. The resultant pulp by the use of formaldehyde or acetone is better with respect to brightness and other critical properties. The viscosity and strength

properties further enhanced at reduced oxidizing chemical doses at similar level of brightness to control. There is no yield loss and the overall cost for formaldehyde addition works out to be lower by Rs. 63.80/T of B.D. pulp on $\rm H_2O_2$ or Rs. 21.20/T of B.D. pulp in $\rm CIO_2$. Industrial application is possible with proper storage and dosing mechanism on which the institute is working upon.

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REFERENCES:

 Al-Dajani, W.W., Jiang, Z.H., Berry R. and Van Lierop B.; "The optimum pH for aldehydeenhanced bleaching" International pulp bleaching

TABLE – 5: COST BENEFIT DUE TO H₂O₂ SAVING BY USE OF FORMALDEHYDE

Sl. No.	Particulars	Unit	Usage	Value (Rs.)
1.	Rate of formaldehyde (40%)	Rs./kg	22.0	-
2.	Dosage	kg./T	7.5	165.00
3.	Rate of H ₂ O ₂ (50%)	Rs./kg	22.0	-
4.	Reduction in H ₂ O ₂	kg./T	10.4	228.80
5.	Net saving (4-2)	Rs./T	-	63.80

$\frac{\text{TABLE} - 6: \text{COST BENEFIT DUE TO ClO}_2 \text{ SAVING BY USE OF}}{\text{FORMALDEHYDE}}$

Sl. No.	Particulars	Unit	Usage	Value (Rs.)
1.	Rate of formaldehyde (40%)	Rs./kg	22.0	-
2.	Dosage	kg./T	7.5	165.00
2.	Cost of ClO ₂	Rs./kg	70.0	-
3.	Reduction in ClO ₂	kg./T	2.66	186.20
4.	Net saving (4-2)	Rs./T	-	21.20

- conference, Quebec City, QC, Canada 2-5 June, P21 (2008).
- Al-Dajani, W.W., Jiang, Z.H., Berry R. and Van Lierop B.; "The chemistry of aldehyde-enhanced bleaching" Tappi Engineering, pulping and environmental conference, Jacksonville, FL, USA, P 21

(2007).

- Jiang, Z.H., Van Lierop, B., Berry, R., Audet, A., Thompson, R., Tenhaeff, S., Valach, D., Kosacki, P., O'Bannon, J. and Blake, R.; "The first mill trial of aldehydeenhanced bleaching" International pulp bleaching conference, Stockholm, Sweden, P.206 (2005).
- Yoon, B.H. and Wang, L.J.; "Ionization of ClO₂ in chlorine dioxide delignification" Internal pulp bleaching conference, SPCI, Helsinki, P 407 (1998).
- Seger, G.E., Jameel, H. and Chang, H.M.; "A two-step high-pH/lowpH method for improved efficiency of D-stage bleaching", Tappi 75 (7): 174 (1992).
- Dence, C.W., Reeve, D.W., "Pulp Bleaching Principles and Practice", Tappi Press, P.245, 251 (1996).
- Jiang, Z.H., Van Lierop, B. and Berry R.; "Improving chlorine dioxide bleaching with aldehydes" Tappi International pulp bleaching conference (IPBC), Portland, P 225 (2002).
- 8. Lindgren, B.O., "Chlorine dioxide and chlorite oxidation of phenols related to lignin", Svensk Papperstidn., 74 (3): 57-63 (1971).
- 9. Jiang, Z.H., Van Lierop, B. and Berry, R., "Improving chlorine dioxide bleaching with aldehydes", JPPS, 33 (2): 89-94 (2007).
- 10. Bleaches Chemistry
 Encyclopedia, www.chemistry
 explained.com / Ar-Bp /
 Bleaches.html.
- 11. March, J., Advanced Organic Chemistry (Third Edition), Wiley Eastern Ltd., New Delhi, P 630 (1991).
- 12. Yoon, B.H., Wang, L.J., Yoon, S.L. and Kim, S.J., "Mechanism of chlorate formation in chlorine dioxide delignification", Appita J., 57 (6): 472 (2004).