Additives for Increased Lignin Removal Efficiency in Oxygen Delignification

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ABSTRACT

Oxygen delignification has become very popular for extended pulping. However, it has a major limitation. The delignification is limited to about 50% because of poor selectivity and degradation of carbohydrates beyond this point. Higher removal of lignin, therefore, causes loss of viscosity and pulp strength. It is thus important to look for methods to improve selectivity. This study investigates the use of hydrogen peroxide as an additive in oxygen delignification together with some other chemicals (magnesium sulphate and an organophosphonate) to improve the kappa reduction as well as selectivity. Effects on bleaching chemicals consumption and pulp strength have also been covered. The organophosphonate used was found to be particularly useful as it provided the best selectivity together with removal of transition metals from the pulp.

INTRODUCTION

Oxygen delignification (ODL) has come to be recognized as an indispensable tool for extended pulping. It is an environmentally friendly technology as it enables the recovery of higher percentages of process chemicals since the effluent from the ODL stage can be recycled to the chemical recovery plant. It also reduces bleach plant pollution by reducing the incoming pulp kappa number, which leads to the reduction of bleaching chemicals used.

The Limitations of Oxygen Delignification

It has been shown (1) that almost all the lignin in kraft pulp can be removed with an oxygen stage. However, the degree of delignification is limited to about 50% (2) by the degradation of carbohydrates in the pulp, which results in strength loss if delignification is allowed to proceed beyond certain limits.

The reaction of oxygen with lignin and carbohydrates is complicated (3) due to the generation of many reactive species. The reduction of the oxygen molecule to water (by phenolic hydroxyl groups of lignin for example) could be due to a four-step reaction owing to the formation of reactive radicals and hydrogen peroxide. A possible sequence is :

Oxygen (O_2) $\longrightarrow$ Peroxy Radicals ($HOO^\bullet$) $\longrightarrow$ Hydrogen peroxide (H_2O_2) $\longrightarrow$ Hydroxyl Radicals ($^\bullet OH$) $\longrightarrow$ Water (H_2O)

The intermediate oxidants exist primarily as their conjugate bases under alkaline conditions used for oxygen delignification. The hydroxyl radicals react with both lignin and carbohydrates. They induce random chain breakage in the latter which, if continued, keeps reducing the DP and eventually affects the pulp strength. It may be noted that oxygen is the least reactive of the oxidants present.

Apart from the above, other limitations of oxygen delignification arise from problems with mass transfer (3). Gaseous oxygen needs to be transferred from (i) gas-to-liquid and (ii) liquid-to-solid phases before lignin oxidation can begin. Increasing the mass-transfer areas can be a starting point. However, gas-liquid mass transfer is hindered by the low solubility of oxygen in water (1% of the solubility of chlorine).

Further, the transfer of oxygen in the solid phase (fiber wall) to the lignin molecule and the transfer of the reaction products through the solid phase are both diffusion processes, which are inherently slow.

Improvement of Selectivity

It is widely held (6) that the hydroxyl radical generated as given above, is responsible for carbohydrate degradation. Its formation is also catalysed by transition metals, such as Fe, Cu and Mn.

Strategies to reduce the degradation of carbohydrates by radicals during oxygen delignification include hydrogen peroxide addition (1, 2) and the addition of magnesium sulphate to inhibit the catalytic activity of the transition metals or the removal of these metals by a preliminary acid washing or complexing step (5-8). The management of free transition metals is an important consideration in achieving selectivity in oxygen delignification (4).

Other approaches include the use of radical scavengers (6). However, the concentrations required for effective selectivity improvement were very high. An interesting method of using a radical scavenger has been reported (6) using polymers that adsorb on the cellulose surfaces. In this way, the oxygen radicals may be trapped with relatively small amounts of radical scavengers if they are concentrated at the cellulosic surfaces, thereby acting as a protective layer for the cellulose. This may be achieved with polymers that adsorb on the cellulose surface such as guar galactomannan. This study found about 30% selectivity improvement with the use of 2% guar galactomannan on pulp.

The Present Study

The present work uses hydrogen peroxide as a primary additive and either magnesium sulphate or an organophosphonate as secondary additives. The results have been compared with the effects observed when hydrogen peroxide was used alone. The chemicals were added directly in the oxygen delignification stage and not used as a pretreatment. For comparison, a “blank” has also been done without any additive.

This work further investigates the selectivity obtained with different additives.

- The study also looks into the quantum of reduction of chemicals

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in multistage bleaching as a result of lower kappa numbers from the oxygen stage.

- The content of transition metals has also been studied at different stages, i.e., before and after oxygen delignification with and without additives and after multistage bleaching.
- Finally, the effect of different additives on the strength of the final fully bleached pulp has been evaluated.
- Some comments have also been included on choosing between the additives.

EXPERIMENTAL

Unbleached Pulp: Unbleached pulp from the displacement press (DP1) was collected from JKPM and used for the study. The raw material furnish used was approximately 75% mixed hard woods and 25% bamboo. The pulp was initially washed in a basket centrifuge and shredded by hand before storage in plastic bags. The pulp was tested for kappa number and viscosity and the unbleached brightness was determined using pulp pads made in distilled water. In some cases, the content of transitional metals (Fe, Cu and Mn) were also tested by spectrophotometric methods.

Blank Experiment: A control or 'blank' ODL experiment without any additives was conducted using laboratory conditions standardized earlier in PAPRI. These conditions were:

Unbleached pulp: 400 g od, oxidized white liquor used: 1.5% as NaOH on od pulp, consistency: 10%, temperature: 100 ^{0}C., oxygen pressure: 5 kg/cm^2, retention: 1 hour. The ODL was conducted in a 15-Lit. rotary s.s. digester. At the end of 1 hour, the heating was stopped and pressure released. After measuring the end pH, the pulp was taken out and washed in a basket centrifuge. It was then shredded by hand and stored in a plastic bag.

The following tests were carried out on the ODL treated pulp:

Moisture and pulp yield, kappa number, viscosity, brightness and metal content (Fe, Cu and Mn). Metal contents were determined spectrophotometrically using colourimetric methods. Standard methods were used for the other tests.

The selectivity of the ODL step was also calculated from the data for the unbleached (DP1) and the ODL-treated pulps. The selectivity was defined as the drop in kappa number after ODL divided by the drop in pulp viscosity. This ratio measures the delignification obtained for unit drop in viscosity and is a measure of 'selectivity', that is, lignin removal in relation to carbohydrate degradation. The higher this ratio, the greater is the delignification and the lower is the carbohydrate attack during the ODL step.

The experimental data are given in Table 1.

The above procedure was followed for all the ODL experiments conducted in this study.

ODL With Additives: The primary additive used in the ODL stage was hydrogen peroxide.

The peroxide stabilizers evaluated as secondary additives for this application were:

- Magnesium Sulphate
- M-760 Organophosphonate (Samples were obtained through the courtesy of M/s Aquapharm Chemicals Pvt. Ltd., Pune)

The experimental data have been given in Table 1. Figures for peroxide addition refer to 100% peroxide. M-760 was added on as received basis and mixed with oxidized white liquor before addition.

Multistage Bleaching: Selected ODL-treated pulps were fully bleached by the sequence C/D EOP D to brightness levels of 88-89 %ISO. The aim in these studies was to determine whether it would be possible to reduce chlorine dioxide usage in the D stage by taking advantage of the lower kappa

TABLE - 1: EFFECT OF DIFFERENT ADDITIVES IN THE ODL STAGE ON PULP QUALITY AND METAL CONTENT

Sl. No.	Particulars	Unit	DP1 Pulp	Blank	Only 0.20% H_2O_2	0.20% H_2O_2 0.05% $MgSO_4$	0.30% H_2O_2 0.05% $MgSO_4$	0.20% H_2O_2 0.05% M-760	0.20% H_2O_2 0.07% M-760
1	OD pulp	gm.	-	400	400	400	400	400	400
2	Oxidized white liquor	% as NaOH on pulp	-	1.5	1.5	1.5	1.5	1.5	1.5
3	**Additives :**		-						
	H_2O_2	% on pulp	-	-	0.2	0.2	0.3	0.2	0.2
	$MgSO_4$	% on pulp	-	-	-	0.05	0.05	-	-
	M-760	% on pulp	-	-	-	-	-	0.05	0.07
	HP-100	% on pulp	-	-	-	-	-	-	-
4	Consistency	%	-	10	10	10	10	10	10
5	Temperature	^{0}C	-	100	100	100	100	100	100
6	O_2	Kg/cm^2	-	5	5	5	5	5	5
7	Retention	hr.	-	1	1	1	1	1	1
8	End pH	-	-	10.4	10.4	10.2	10.1	10.4	10.4
9	Yield	%	-	95.6	95.5	96.3	96	96.5	96.6
10	Kappa no.	-	17.5	12.1	10.5	10.6	10.2	10.6	10.6
11	Kappa reduction	%	-	30.8	40.0	39.4	41.7	39.4	39.4
12	Viscosity	cP	14.4	11.9	11.8	12.1	11.8	12.3	12.4
13	Brightness	% ISO	28.4	37.8	40.5	40.4	41.2	40.3	40.4
14	Selectivity*	-	-	2.2	2.69	3	2.8	3.28	3.45
15	**Metals :**								
	Fe	ppm	34.8	31.9	28	28.1	25.12	24.93	24.1
	Fe reduction	%	-	8.4	19.5	19.3	27.8	28.4	30.8
	Mn	ppm	0.984	0.8	0.58	0.76	0.562	0.307	0.232
	Mn reduction	%	-	19.7	41.1	22.8	42.9	68.8	76.4
	Cu	ppm	0.286	0.2	0.142	0.144	0.104	0.134	0.116
	Cu reduction	%	-	47.2	50.4	49.7	63.6	53.2	59.4

$$* \text{ Selectivity} = \frac{\text{Drop in kappa in ODL}}{\text{Drop in Viscosity}}$$

S. NO.	PARTICULARS	UNITS	DP1 PULP	BLANK ODL	REDUCTION, %
1.	Kappa No.	-	17.5	12.1	30.8
2.	Viscosity	cP	14.4	11.9	17.4
3.	Selectivity	-	-	2.2	-
4.	Brightness	%ISO	28.4	37.8	-
5.	Yield	%	-	95.6	-
6.	Fe	ppm	34.8	31.9	8.4
7.	Mn	ppm	0.98	0.8	19.7
8.	Cu	ppm	0.29	0.2	47.2

TABLE - 2 : MULTISTAGE BLEACHING DATA

Sl. No.	Stages	Bleaching Condition	Particulars	Unit	Blank	Only 0.20% H_2O_2	0.20% H_2O_2 0.05% $MgSO_4$	0.30% H_2O_2 0.05% $MgSO_4$	0.20% H_2O_2 0.05% M-760	0.20% H_2O_2 0.07% M-760
1	ODL stage		Brightness	% ISO	37.8	40..5	40.4	41.2	40.3	40.4
			Kappa No. after ODL	-	12.1	10.5	10.6	10.2	10.6	10.6
			Viscosity	cP	11.9	11.8	12.1	11.8	12.3	12.4
2	CD stage		End pH	-	2.8	2.5	3.2	2.7	2.8	2.5
			Residual Cl_2	ppm	28.4	14.2	28.4	42.6	28.4	21.3
			Cl_2 applied as Cl_2	%	3.44	2.9	2.93	2.83	2.93	2.93
			ClO_2 applied as Cl_2	%	0.65	0.65	0.65	0.65	0.65	0.65
			Cl_2 consumed as Cl_2	%	4.06	3.54	3.55	3.39	3.55	3.56
			Kappa number	-	4	3.7	3.5	3.2	3.6	3.5
		Cy% : 10	Viscosity	cP	10	10.1	10.4	10.2	10.8	10.8
		Temp.: Amb.	Brightness	% ISO	55.8	57.4	57	57.8	56.8	57.7
		Time: 1 hr.	L	-	81.81	82.80	82.42	83.01	82.2	82.95
			a	-	0.88	0.48	0.61	0.52	0.61	0.42
			b	-	10.21	9.35	9.81	9.24	10.03	9.26
			WI	-	17.88	19.48	18.86	19.61	19.01	19.68
			YI	-	18.26	17.65	17.88	17.41	17.98	17.48
			ΔB	-	-0.06	-0.07	-0.09	-0.07	-0.09	-0.07
3	EOP stage		End pH	-	11	11.4	11	11.2	11.2	11.4
			Kappa number	-	1.5	1.4	1.2	1.1	1.2	1.1
		Cy% : 10	Viscosity	cP	8	8.1	8.5	8.2	9	8.8
		Temp.: 80 ^{O}C	Brightness	% ISO	77.6	78.4	78.4	78.8	78.2	78.6
		Time: 1.5 hr.	L	-	92.01	93.02	92.91	93.11	92.64	93.18
		Alkali: 2%	a	-	0.41	0.32	0.38	0.38	0.4	0.3
		H_2O_2: 1.5%	b	-	6.34	5.68	5.91	5.61	6.01	5.51
		O_2: 2 kg/cm^2	WI	-	54.11	55.75	55.12	55.98	55.01	55.91
			YI	-	9.98	8.82	9.48	8.68	9.61	8.96
			ΔB	-	0.01	0.3	0.2	0.3	0.2	0.3
4	D stage		End pH	-	3	3.0	3.2	3	2.8	3.1
			Residual Cl_2	ppm	142	142	142	185	156.2	156.2
			ClO_2 applied as Cl_2	%	2.2	1.91	1.93	1.85	1.93	1.93
			ClO_2 consumed as Cl_2	%	2.06	1.76	1.79	1.66	1.77	1.77
			Total Cl_2 applied as Cl_2	%	6.292	5.46	5.512	5.304	5.512	5.56
			Total Cl_2 consumed as Cl_2	%	6.12	5.3	5.34	5.05	5.32	5.33
		Cy% : 10	Viscosity	cP	7.6	7.6	8.1	7.8	8.5	8.4
		Temp.: 70 ^{O}C	Shrinkage	%	9.2	9.3	8.5	9	8	8
		Time: 4 hr.	Yield	%	90.8	90.7	91.5	91	92	92
			Brightness	% ISO	88.6	88.8	88.8	88.9	88.8	88.9
			L	-	94.81	95.16	95.08	95.32	95.01	95.31
			a	-	-0.01	-0.02	-0.02	-0.02	-0.01	-0.03
			b	-	3.6	3.25	3.36	3.09	3.34	3.15
			WI	-	76.01	77.1	76.8	77.2	76.8	77.32
			YI	-	4.68	4.27	4.4	4.05	4.42	4.1
			ΔB	-	0.4	0.6	0.6	0.85	0.6	0.7
			P.C No	-	1.05	0.81	0.81	0.72	0.72	0.76
			Ash	%	0.76	0.71	0.71	0.62	0.52	0.41
5	Metal content		Iron	%	18.7	14.8	14.9	13.6	11.6	11.5
			Iron reduction	%	-	20.9	20.3	27.3	38.0	38.5
			Manganese	%	0.25	0	0	0	0	0
			Manganese reduction	%	-	100.0	100.0	100.0	100.0	100.0
			Copper	%	0.057	0.045	0.049	0.044	0.034	0.031
			Copper reduction	%	-	21.1	14.0	22.8	40.4	45.6

NOTE: Total Cl2 added = 0.52 x Kappa No. after ODL

number of the ODL-treated pulps. Reduction of chlorine dioxide would improve the economics of additive use in the ODL stage.

Laboratory multistage bleaching was done as follows: C/D stage in plastic buckets, EOP stage in rotary s.s. digester and D stage in plastic bags placed in a temperature-controlled water bath at 70 ^{0}C. The pulps were washed in a basket centrifuge. All bleached pulps were tested for brightness, shrinkage, viscosity, PC no., metal content and strength properties after beating in a Valley beater to 40 ^{0}SR and preparing standard handsheets.

Experimental conditions and results of multistage bleaching have been given in Table 2. Pulp strength properties have been presented in Table 3.

RESULTS AND DISCUSSION

Oxygen Delignification (ODL) Studies:

Blank ODL: Reference to Table 1 gives the characteristics for the DP1 pulp and the ODL-treated pulp using the standard PAPRI conditions (blank) without additives as Listed below Table 1.

It may be seen that the kappa number reduction without additives was 30.8% with a selectivity of 2.2. The pulp yield was 95.6% at a kappa of 12.1. The brightness improved by 9.4 points. The transition metal content also reduced, the maximum reduction being observed in the case of copper (47.2%) followed by manganese (19.7%). Iron content was only slightly reduced by about 8.4%.

Effect of Peroxide Addition: The addition of 0.2% hydrogen peroxide on pulp (2kg/T of pulp) during the ODL stage immediately reduced the kappa number to 10.5 from 12.1 obtained earlier. This is a reduction of 40% against 30.8% in the blank. The viscosity was observed to drop marginally to 11.8 cP (blank 11.9). The selectivity improved to 2.69 from 2.2 in the blank. The pulp yield was 95.5% (blank 95.6%). Brightness improved to 40.5% ISO, which is 2.7 points higher than the blank.

Thus, addition of peroxide was observed to improve the delignification (kappa reduction) in the ODL stage by about 10% compared to the blank. The selectivity also improved indicating lower carbohydrate degradation in spite of the higher lignin removal. The brightness also increased compared to the blank. Thus peroxide addition definitely improved the ODL stage performance.

The content of transition metals in the pulp reduced on the use of hydrogen peroxide, which could be because of reaction with peroxide. The reduction of all metals, Fe, Mn and Cu, was more than in the blank (Table 1).

Effect of Peroxide+$MgSO_4$: When the peroxide was supplemented by the addition of 0.05% $MgSO_4$ on pulp (0.5 kg/T), the kappa reduction came to 39.4%, which was slightly lower than with peroxide alone. However, there was a fairly large improvement in selectivity, which increased to 3.0 from 2.69. The brightness was also maintained at 40.4% ISO while the yield increased to 96.3% from 95.5%, which was clearly due to improved carbohydrate retention. The viscosity also improved to 12.1 cP from 11.8 with peroxide alone. Compared to the blank, the viscosity was slightly higher even though the kappa reduction had increased from 30.8 to 39.4%. Thus, MgSO4, a classical additive for peroxide bleaching, proved to be useful when added with hydrogen peroxide in the ODL stage as well.

Increasing the peroxide charge to 0.3% while maintaining the $MgSO_4$ dose at

S. NO.	PARTICULARS	UNITS	BLANK	H2O2+0.05% M-760	H2O2+0.07% M-760
1.	Kappa No.	-	12.1	10.6	10.6
2.	Kappa Reduction	%	30.8	39.4	39.4
3.	Viscosity	cP	11.9	12.3	12.4
4.	Brightness	% ISO	37.8	40.3	40.4
5.	Selectivity	-	2.2	3.28	3.45
6.	Fe Reduction	%	8.4	28.4	30.8
7.	Mn Reduction	%	19.7	68.8	76.4
8.	Cu Reduction	%	47.2	53.2	59.4

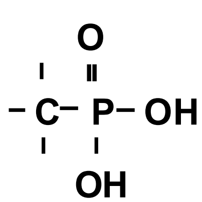
S. NO.	PARTICULARS	UNITS	UNBLEACHED (DP1) PULP	OXYGEN DELIGNIFICATION			
				BLANK	ONLY 0.2% H_2O_2	0.2% H_2O_2 + 0.05% $MgSO_4$	0.2% H_2O_2 + 0.05% M-760
1.	Kappa no.	-	17.5	12.1	10.5	10.6	10.6
2.	Kappa reduction	%	-	30.8	40.0	39.4	39.4
3.	Viscosity	cP	14.4	11.9	11.8	12.1	12.3
4.	Brightness	% ISO	28.4	37.8	40.5	40.4	40.3
5.	Selectivity	-	-	2.2	2.69	3.0	3.28
6.	Fe reduction	%	-	8.4	19.5	19.3	28.4
7.	Mn reduction	%	-	19.7	41.1	22.8	68.8
8.	Cu reduction	%	-	47.2	50.4	49.7	53.2
9.	Pulp yield	%	-	95.6	95.5	96.3	96.5

0.05% increased the kappa reduction and marginally increased the brightness but reduced the yield, selectivity and viscosity.

With 0.2% peroxide the content of transition metals was found to be lower than in the blank. Higher metal reduction was observed with 0.3% peroxide. It is likely that more metals were removed at 0.3% dose by reaction with peroxide without increasing the brightness significantly.

Peroxide + an Organophosphonate, M-760:

Organophosphonates are a class of organic compounds containing carbon-phosphorus bonds. The phosphonate group is made up of a central phosphorus atom linked respectively to two hydroxyl groups, one oxygen atom and a carbon atom, giving a structural formula:



M-760 is a formulation based on selected organophosphorous compounds exhibiting excellent properties for chelation of metal ions. It is a good peroxide stabilizer and dispersing and deflocculating agent. Application in the ODL stage is a new application for this product.

M-760 was applied in two doses, 0.05 and 0.07% on od pulp. In each case, 0.2% peroxide was added on pulp. The effect of using M-760 is summarized in the table above (Top):

The table shows that there is not much difference between the two M-760 doses when used with 0.2% peroxide. The kappa reduction, viscosity and brightness are at similar levels. The selectivity and metal reduction are slightly better with 0.07% dose.

When compared with the other additives tried earlier, it can be observed from Table 1 that the kappa reduction is the same as that with $MgSO_4$ but slightly less than that with H_2O_2 alone. The brightness is marginally lower for M-760 compared to both $MgSO_4$ and H_2O_2 alone. However, the pulp viscosity is significantly higher with M-760 indicating better carbohydrate preservation. The selectivity with M-760 (3.28) was also the highest among all the additives and is a result of less carbohydrate degradation. Consequently, the yield is also the highest, 96.5%, although the use of $MgSO_4$ also gives high yield, 96.3%. The use of H_2O_2 alone without any additive gives lower yield (95.5%) which is similar to the blank (95.6%).

Reduction figures for the three transitional metals, Fe, Mn and Cu were also the highest for M-760, indicating its much superior sequestering properties in comparison to $MgSO_4$.

The table on the left (down) summarises the data collected and discussed above.

Multistage Bleaching

All ODL treated pulps were subjected to multistage bleaching by the sequence C/D EOP D. The brightness target was 88-89 %ISO. The bleaching data are given in Table 2.

The results show that, at every stage of multistage bleaching, the pulps treated with peroxide and M-760 during ODL outperformed $MgSO_4$. M-760 treated pulps delivered the highest bleached yield (lowest shrinkage), highest viscosity and comparable brightness. The reduction of transition metals Fe, Mn and Cu was the highest with the use of M-760. Also, it may be noted that the use of a higher dose of M-760, 0.07%, did not bring significant additional benefits.

Another advantage with the use of M-760 during the ODL stage was that, after multistage bleaching, these pulps had the most stable brightness (lowest PC No.), lowest ash content and correspondingly lowest transition metal content (Fe, Mn and Cu) among all the pulps. This low content of colour-causing transition metals could be beneficial for reducing dye/optical brightener consumption in the paper machine area.

It appears from the above that the benefits obtained with the use of M-760 in the ODL stage were continued in multistage bleaching as well.

Other points of interest seen from Table 2 are:

- The use of 0.3% peroxide (instead of 0.2%) with $MgSO_4$ in the ODL stage produced almost the same brightness after multistage bleaching but increased shrinkage and reduced the viscosity.
- The use of 0.2% peroxide without any additive in the ODL stage

adversely affected the multistage bleaching results. The brightness target was reached (88.8% ISO) but the yield reduced due to higher shrinkage. The viscosity also reduced. Thus, protection of hydrogen peroxide with an additive is essential in order to get the best results.

Bleaching Chemical Consumption

Reduction of the kappa number after the ODL stage through the use of additives like M-760 and $MgSO_4$ with H_2O_2 has another advantage during multistage bleaching. The bleach demand reduces due to the lower lignin level in the pulp. The extent of this reduction and its effect on bleached pulp properties is shown in the table on the right (Top):

S. NO.	PARTICULARS	UNITS	BLANK	ONLY H_2O_2	H_2O_2+$MgSO_4$	H_2O_2+M-760
1.	Kappa After ODL	-	12.1	10.5	10.6	10.6
2.	Brightness	%ISO	37.8	40.5	40.4	40.3
3.	Viscosity	cP	11.9	11.8	12.1	12.3
4.	Total Cl_2 Applied	% on od pulp	6.3	5.46	5.5	5.5
5.	Cl_2 Reduction on Blank	%	-	13.2	12.7	12.7
6.	Brightness	%ISO	88.6	88.8	88.8	88.8
7.	Viscosity	cP	7.6	7.6	8.1	8.5
8.	Bleached Yield	%	90.8	90.7	91.5	92.0

This table shows that the total chlorine (including chlorine dioxide) applied for multistage bleaching can be reduced by about 12-13% with the use of additives in the ODL stage which brings down the post ODL kappa number. Even with this reduced chlorine charge, the final brightness is consistently higher than the blank. The viscosity is also higher than the blank. The bleached yield is also higher when $MgSO_4$ or M-760 are used in the ODL stage.

It should be mentioned here that, although the chlorine demand is low even for the pulp obtained with only H_2O_2 added in the ODL stage, this pulp gets no carbohydrate protection due to the absence of the secondary additives. Hence, even though the brightness is high, the pulp yield and viscosity are both significantly less than those for $MgSO_4$ or M-760.

Bleached Pulp Strength

Table 3 shows the strength properties of the bleached pulp prepared from ODL pulp treated with different additives. The following observations were made:

TABLE - 3 : STRENGTH PROPERTIES OF FINAL BLEACHED PULP

Sl. No.	Properties	Unit	Blank	Additives used: Only 0.20% H_2O_2	0.20% H_2O_2 0.05% $MgSO_4$	0.30% H_2O_2 0.05% $MgSO_4$	0.20% H_2O_2 0.05% M-760	0.20% H_2O_2 0.07% M-760
1	Brightness	% ISO	88.6	88.8	88.8	88.9	88.8	88.8
2	Initial freeness	^{O}SR	18	18	18	18	18	17
3	Beating time	minute	27	28	30	27	32	33
4	Thickness	µm	78.6	79.6	78.3	79.9	79.3	79.3
5	Breaking length	mtr.	6722	6831	6974	6773	7133	7155
6	Burst factor	-	51	53	55	51	56	56
7	Tear factor	-	63	60	63	60	59	55
8	Double fold	no.	37	39	41	40	44	42

The best increase in strength properties over the blank was obtained with the use of M-760 (0.05%) and peroxide (0.2%). Increasing the dose of M-760 to 0.07% did not improve the strength much. The next most effective additives were peroxide (0.2%) and $MgSO_4$ (0.05%). Here again, increasing the peroxide dose to 0.3% was found to reduce the pulp strength. Using only 0.2% peroxide without a supporting additive also reduced the strength compared to the pulp prepared with peroxide and $MgSO_4$.

From the point of view of overall bleached pulp strength, M-760 (0.05%) and hydrogen peroxide (0.2%) have proved to be the best ODL additives followed by peroxide (0.2%) and $MgSO_4$ (0.05%). It should be mentioned that the differences in strength properties, although present, are not very large.

Choosing Between the Additives

This study has looked into the use of the following additives in oxygen delignification :

1. Only hydrogen peroxide (H_2O_2)
2. H_2O_2 and magnesium sulphate ($MgSO_4$)
3. H_2O_2 and a commercial organophosphonate preparation (M-760).

The choice between them will depend upon factors like cost, ease of application, technical considerations, likely process problems, etc.

- In terms of cost, using only H_2O_2 would be the cheapest option followed by H_2O_2 and $MgSO_4$. The use of H_2O_2 and M-760 would be the most expensive. The estimated costs based on 2007 prices would be approximately in the ratio of 1 (only H_2O_2) : 1.17 (H_2O_2 + $MgSO_4$) : 1.47 (H_2O_2 + M-760).
- The use of secondary additives with H_2O_2 in oxygen delignification gives certain additional benefits which are summarized on next page (Top) in comparison to H_2O_2 alone.
- The use of secondary additives with H_2O_2 in oxygen delignification gives additional benefits in multistage bleaching, final metal content and pulp strength(next page bottom) :
- Process problems are not expected with the use of either H_2O_2 alone or H_2O_2 with M-760. In fact, with the use of M-760, more metals are solubilised and the deposit problems in multiple-effect evaporators are likely to be reduced. Further, both are liquids and no handling or dosing problems are anticipated.
- In contrast, $MgSO_4$ is a solid. The use of this will involve additional cost due to handling, feeding, dissolving, etc. Further, the addition of 0.05% $MgSO_4$ on pulp will mean the input of 0.5 kg of $MgSO_4$ per tonne of pulp or about 4.5 tonnes of $MgSO_4$ per month for

Sl. No.	Particulars	H_2O_2 + $MgSO_4$	H_2O_2 + M-760
1.	Kappa no. reduction	Marginally higher to H_2O_2	Marginally higher to H_2O_2
2.	Selectivity	Higher	Highest
3.	Viscosity	Slightly higher	Highest
4.	Brightness	Marginally lower	Marginally lower
5.	Yield	Higher	Highest
6.	Fe reduction	Similar	Significantly better
7.	Mn reduction	Poor	Very high
8.	Cu reduction	Similar	Best

Sl. No.	Particulars	H_2O_2 + $MgSO_4$	H_2O_2 + M-760
1.	Total chlorine applied	Same as H_2O_2 alone	Same as H_2O_2 alone
2.	Viscosity	Higher	Highest
3.	Shrinkage	Lower	Lowest
4.	Brightness	Same	Same
5.	Iron reduction	Slightly less	Highest
6.	Manganese reduction	This was 100% in all cases, including the use of H_2O_2 alone.	
7.	Copper reduction	Lower	Highest
8.	Bleached pulp strength	Slightly better	Slightly better

a 300 TPD mill to the pulp mill recovery causticizing liquor system. There is a possibility of $Mg(OH)_2$ precipitation in the causticising area.

On balance, it is felt that individual mills will have to consider all the above factors, conduct plant trials and decide on the additive/s which would be best for them.

CONCLUSIONS

- The use of hydrogen peroxide as an additive in the oxygen delignification (ODL) of mixed hardwoods and bamboo pulp has been found to accelerate delignification and increase the kappa number reduction.
- There was some tendency for viscosity reduction after ODL with the use of peroxide and loss of selectivity. This could be avoided by the use of a second additive. These compounds helped to reduce the viscosity drop, improved the selectivity in some cases and increased the pulp yield.
- The content of transition metals was also found to reduce with the use of hydrogen peroxide. Some secondary additives helped to further reduce the metal content of the pulp.
- The following combinations of hydrogen peroxide and secondary additives were found useful:

1. 0.2% peroxide with 0.05% $MgSO_4$.
2. 0.2% peroxide with a commercial organophosphonate compound, M-760 (0.05%)

- In terms of kappa reduction in the ODL stage, the best result was obtained with M-760 closely followed by $MgSO_4$. However, viscosity and yield were the highest with M-760 closely followed by $MgSO_4$. In terms of transition metal reduction, M-760 was the best while $MgSO_4$ gave lower and similar results.
- Further, because of the increased kappa number reduction with the use of additives, the chlorine demand for full bleaching reduced proportionately. It was observed that 12-13% total chlorine demand could be reduced by using additives in oxygen delignification. This will have a very beneficial impact on reducing the pollution from bleach plant effluents.
- The benefits obtained with M-760 were sustained through full bleaching with the sequence C/D-EOP-D. Compared to $MgSO_4$, it was better in terms of final yield, viscosity, brightness and brightness stability (PC number) and the lowest content of transition metals. The low metal content could be useful in reducing the dye and optical brightener use in the paper machine area.
- In terms of bleached pulp strength, the difference between different secondary additives was not very high. M-760 produced slightly better strength properties compared to $MgSO_4$.
- Thus, a new additive has been introduced in this study for improved delignification in the ODL stage. This is a commercial organophosphonate product, designated M-760. M-760 has proved very effective in conjunction with hydrogen peroxide in increasing the kappa number reduction during the ODL stage. Simultaneously, the pulp yield and selectivity also increase.
- The choice of the secondary additives can be decided by individual mills after considering techno-economic factors and taking plant trials.

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