Peroxide Spray Bleaching of CEHH Bleached Pulp

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SUMMARY

By means of a peroxide spray bleaching liquor applied, on laboratory scale, just before simulated flash drying to a CEHH bleached bamboo kraft pulp, it is possible to lift the brightness during storage by about 4 points up to 82-83° ISO.

The addition of phosphates, silicate and DTPA in the bleaching liquor is studied.

Peroxide spray bleaching gives better results than a peroxide bleaching stage in tower added at the end of the CEHH sequence.

INTRODUCTION

Bleaching of a bamboo kraft pulp by a CEHH sequence leads to final brightness of about 78° ISO (80° Photovolt). As expected after hypochlorite stages, final brightness is not stable, and drops to some 74° ISO (76° Photovolt) after 2 to 3 months storage time.

For a market pulp, it would be interesting to keep the brightness level stable during storage. Better still would be to increase the brightness by 2 to 3° PV and to maintain this gain stable during 2 to 3 months. Achieving this objective would greatly improve pulp quality.

THE AGEING PROBLEM OF BLEACHED CHEMICAL PULPS

Brightness reversion has been the purpose of a great number of studies and if it is well established that residual lignin in the bleached pulp has a prevailing influence on it, a lot of different factors contribute to pulp yellowing.

Amongst these factors, we could mention :

—bleach residues (chlorinated organic compounds for instance, mainly after H stages)

—natural resins and vegetal waxes or their derivatives

—metal contaminants : Cu, Mn .....

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It is well known that hypochlorite stages lead to well marked brightness lifts, but on the other hand this brightness is not stable.

On the contrary, peroxide very often does not give such important brightness gains, especially if it is applied just after an H stage, but the resultant brightness is much more stable.

Bleached kraft pulp still contains a small amount of residual lignin, and during storage, a partial oxidation of this lignin gives coloured compounds.

The problem of brightness reversion has been frequently studied 1,2,3,4,5.

Two types of components are often mentioned in the literature as responsible for this yellowing. One of the reactions which may occur involves the aromatic ring, giving benzoquinone type derivates (Fig. 1 Reaction I). Also mentioned are reactions involving side chain and giving for instance in the phenyl propane units carbonyl functions conjugated with the aromatic ring (Figure I Reaction II). In each of these cases a further oxidation of the formed compounds leads to leucoderivatives. Thus benzoquionones will be oxidised to diacids, and compounds having a carbonyl group in a–position of the aromatic ring will be split as indicated in figure 1.

Reactions involving residual lignin in pulp are very complex and incompletely known, and cannot be limited to these two examples.

PEROXIDE BLEACHING IN TOWER

To limit as much as possible brightness reversion, which is particularly important in the case of a bleached bamboo kraft pulp because of the presence of two hypochlorite stages (sequence CEHH), our first idea was to introduce a peroxide stage in the sequeace, preferably at the last step.

Using a sample of crude kraft pulp, we have carried out, on laboratory scale, some comparative trials according to the following sequences (see figure 2) :

CEHH as reference	(sequence 1)
CEHHP	(sequence 2)
CEHP	(sequence 3 and 4)

Examination of the results shows that in this case a brightness of 80.80° ISO can be obtained by the CEHH sequence, but reversion is very important : PC = 10.01 (Post colour number after dry ageing at 105°C for 24 h .

If a P stage using 0.3% H_2O_2 is added to this sequence, brightness stability is improved.

If the last stage of the CEHH sequence is replaced by a P stage, leading to a saving of 30% NaClO, the brightness is lower but stability is improved.

Finally, if all the hypochlorite used in the CEHH sequence is introduced at the third stage, and the last stage of the sequence is converted to a P stage using 0.3% H_2O_2, final brightness and stability are as good as for CEHHP. Meanwhile, a drop of mechanical properties of the pulp can be expected due to a more marked cellulose degradation because of the high dose of active chlorine introduced in a single step.

As a conclusion these results are disappointing. The bleaching action of the peroxide in this case is small or null; it seems that physico-chemical conditions of tower bleaching are not sufficient to activate the hydrogen peroxide.

Consequently we have looked for a different action of peroxide from the usual tower bleaching system, an action which could be more efficient against brightness reversion during storage.

PEROXIDE SPRAY BLEACHING

The spray bleaching technique is not new. It has already been studied in the laboratory and also applied on mill scale for different types of pulp 6,7,8,9.

PRINCIPLE

The pulp, pressed to 50% consistency, is sprayed with a peroxide bleaching liquor, then dried at high temperature and then baled. As drying is normally quite quick, a substantial amount of peroxide can remain in the baled pulp. During storage, the bleaching action of the peroxide will develop further with the time and counteract the normal tendency of the pulp to revert in brightness (see figure 1 : oxidation of chromophores into leucoderivatives, whereas spontaneous oxidation without peroxide leads to coloured compounds).

In this type of bleaching, the very high consistency of the pulp and the long retention time during storage are certainly favourable to peroxide activity.

TECHNICAL ASPECT ON MILL SCALE

This post bleaching study of a bleached kraft pulp has been considered in the case of a plant having a flash dryer.

The various steps concerned by the bleaching technique are usually the following ones :

—thickening to 50% consistency

—fluffing of the wet pulp

—flash drying where the pulp is heated very quickly and brought at the same time to about 90% dryness.

—baling.

In such a process, spraying of the pulp would have to take place after thickening to 50% and before fluffing.

It seems very important to distribute very homogenously the bleaching liquor on the pulp at 50% consistency. To obtain a good uniformity on mill scale, we suggest to spray either onto the wet mat of pulp leaving the thickener at 50% consistency or in the conveyer (screw feeder or belt) going from the thickener to the fluffer 7,9.

Fluffing itself will greatly contribute to obtaining a good uniformity of chemicals in the pulp. If good distribution of chemicals is not obtained prior the flash drying, it is unlikely that this homogenisation will occur after drying.

EXPERIMENTS IN THE LABORATORY

The procedure applied on the small scale is given in appendix. We have first prepared in the lab, by a similar CEHH sequence as applied on mill scale, a sample, of bleached pulp (Figure 3).

For this purpose, we have used a sample of bamboo kraft pulp having the same origin as the

one which was used for the preliminary trials (Figure 2), but not sampled at the same time. This can explain some brightness deviations.

The bleached pulp, which had a brightness of 78° ISO (equivalent to 80° P.V.) instead of 80.8° (Figure 2), was washed after the last stage but not acidified. Due to this, the pulp maintained a slight residual alcalinity (pH between 7 and 8).

With a view to preserving as long as possible some peroxide in the pulp, it is normally useful to add stabilizers to the spray liquor. These additives are expected to complex metal traces such as Fe, Cu, Mn, which could catalytically decompose peroxide. Some stabilizers have, in addition, buffering properties which could be useful for peroxide activity. Meanwhile, it is necessary to avoid a too marked alkalinisation which could be expected to accelerate peroxide consumption at the beginning of the storage time, so that later on the pulp will obviously be at an alkaline pH without oxidant, which implies conditions favourable for brightness reversion.

The four following stabilizers have been tested in this study :

—DTPA : sodium diethylene triamine penta acetate

—Silicate 38° Be : water glass : specific gravity : 1.37 $\frac{SiO_2}{Na_2O}$: = 3.3

—$Na_5P_3O_{10}$; sodium tripolyphosphate

—Na_3PO_4 : sodium orthophosphate

Eight different formulations have been tried (Figure 4). For the first one, only peroxide was used, without any stabilizer. For all the other formulations, one or several of the above mentioned stabilizers were used.

For each trial and also for bleached pulp which has not been sprayed and which is taken as reference, we have measured the brightness during 3 month's storage at room temperature (20-25°C).

Peroxide consumption was also measured, first just as the pulp leaves the dryer and later after 90 days storage time.

RESULTS

First it will be noted that the drop in brightness of the kraft pulp bleached by the CEHH sequence during storage is rather important as expected. The brightness loss is about 2° ISO during the first two weeks and 4.6° ISO after 3 months.

For all the trials (Figure 4) it may be remarked that brightness of the pulp as it comes out of the dryer is lower than the final brightness after CEHH. This is due to the fact that the reversion during flash drying is more important than the bleaching action during this short period. But during storage of the dried pulp, the bleaching action of peroxide takes place, and most of the brightness gain is realized during the first 15 days.

We have checked the reproducibility of the spray bleaching trials. The evolution of two identical trials is very similar, in general brightness deviation is only from 0.3 to 0.5° ISO.

The use of spray liquor containing peroxide only (Figure, 4 trial 1) gives a lift of brightness of 26° ISO after 15 days, but later the brightness drops due to complete peroxide consumption. We would expect from an appropriate peroxide stabilization to avoid this reversion. For the formulations of the trials 2 to 8 (Figure 4) buffers and/or stabilizers have been used.

The following trials : 3, 5, 6 and 7 (Fig. 5) may be considered as similar. They all give interesting results, showing a final brightness of 82 to 83° ISO which corresponds to a gain of 4 to 5° ISO after the CEHH sequence. None of the above mentioned trials shows any brightness reversion; this may be easily explained by a marked peroxide residue even after 3 months' storage time.

With formulation 2, though a brightness lift of 4° ISO may be obtained after 3 months, we note a total consumption of peroxide after this period. Reversion has not yet started, but there is now no more peroxide to prevent it. It may be predicted that brightness could drop if storage is prolonged.

With formulation 8, we already have a brightness reversion after 45 days. By comparison with formulation 7, this could be explained by the alcalinity of Na_3PO_4, which is higher than that of $Na_5P_3O_{10}$. Consequently, we also have a higher activation and lower stability of peroxide which is completely consumed during the 90 days' storage.

Although a good stabilization of peroxide was obtained with formulation 4, the brightness develops too slowly.

In addition to brightness control, we have measured pulp ageing 15 days after spraying peroxide, on handsheets prepared from the stored pulp. It can be seen that the post colour number around 4 is particularly low compared the one measured after CEHH, which is 10 (Figure 2).

CONCLUSION

A peroxide spray applied just before simulated flash dryer on a CEHH bleached bamboo kraft pulp allows the brightness to be increased from 78° ISO up to 82-83° ISO with 0.3% H_2O_2, after a storage time of several weeks. Bleaching develops during the storage of the pulp.

The use of phosphates or silicate, which bring along the buffered alkali and at the same time stabilize the peroxide, is recommended in the bleaching liquor. A sequestering agent can also be needed. Peroxide spray bleaching will only be successful if homogeneity of the chemicals in the pulp is achieved.

This kind of process is very suitable for a market pulp, the brightness of which must be stable during weeks before the pulp is processed at customer site.

Compared with tower bleaching, spray bleaching gives better brightness. This is probably due to the higher consistency of the pulp and to the much longer retention time.

It is worth noting that this kind of bleaching can be adapted to other types of dryer.

The authors would like to thank Mr. J. Schaheys who carried out the laboratory trials.

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APPENDIX

EXPERIMENTAL

SIMULATION OF SPRAY BLEACHING ON LABORATORY SCALE

—Unbleached kraft pulp is first bleached on lab scale by the CEHH sequence described at Figure 3.

—With the handsheet machine, prepare pads of pulp containing 10 g dry pulp. Normally 4 or 5 pads are sufficient for carrying out one spray bleaching trial, depending on the number of samplings required during storage time.

– Place the pads between dry blotters and press in the hydraulic press at 5 bars for several minutes. The weight of the wet pads should now be equal to, or less than 20 g (i.e. consistency equal to, or greater than 50%). If necessary, repeat the pressing with fresh blotters.

—Adjust the pad consistency to 50% by spraying water onto the pads until their weight equals 20 g.

—Spray evenly onto each side of the pad sufficient bleaching liquor to raise the weight by 2.22 g. Thus the spraying ratio is : 22.2g of bleaching liquor for 100g of dry pulp.

—Defiber the pads (now at 45% consistency) in a high-speed homogeniser (domestic type).

—Spread the defibered pulp evenly on the wire basket of the steamer to a depth of 15-20 m/m.

—Insert the pulp (20-25 g dry pulp per charge) into the laboratory steamer regulated at 220°C, dry atmosphere, for 2 min 15 sec. For these trials, we have used a steamer which is normally used for simulation of pad-steam bleaching of textiles.

– The pulp is thus dried to about 85% consistency. Should drying be insufficient in the allowed time, the consistency may be adjusted by supplementary drying of the pulp in a circulating air oven at 35-40°C. This extra low temperature drying has not effect on the pulp bleaching.

—Store the bleached pulp in a plastic sack for subsequent measures of brightness at the desired intervals of storage (see figure 4).

—From the pulp removed from the steamer, remove the equivalent of 5 g of dry pulp and suspend it in about 1.1 of dilute sulphuric acid. Titrate the suspension, without filtration, by iodometry as follows :

* add KI and starch
* titration is carried out with S_2O_3 0.1 N
* if A ml is neeced, H_2O_2 consumption will be :

$$\frac{(\text{initial\% } H_2O_2)-(A \times O{,}O34)}{(\text{initial\% } H_2O_2)} \times 100$$

as a percentage of the dose initially applied.

NOTE ;

On laboratory scale, we have used a spraying ratio of 22 cm^3/100g dry pulp, leading to a drop of consistency of 5% (50% to 45%).

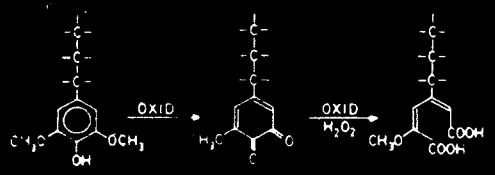
Such a consistency drop could be considered rather high in some plants.

A lower spraying ratio may be adopted if necessary, on condition that uniform impregnation of the chemicals is realized.

In this case, a more concentrated spray liquor will have to be used. We have carried out, without technical problems, mill scale trials with a spraying of 12.5 cm^3/100g dry pulp (a drop of consistency from 50% to 47%).

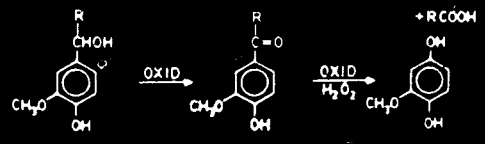
REACTIONS OF RESIDUAL LIGNIN IN KRAFT PULPS

Reaction (I) involving the aromatic ring



Syringyl type compounds — o-benzo quinones (coloured compound) — diacids

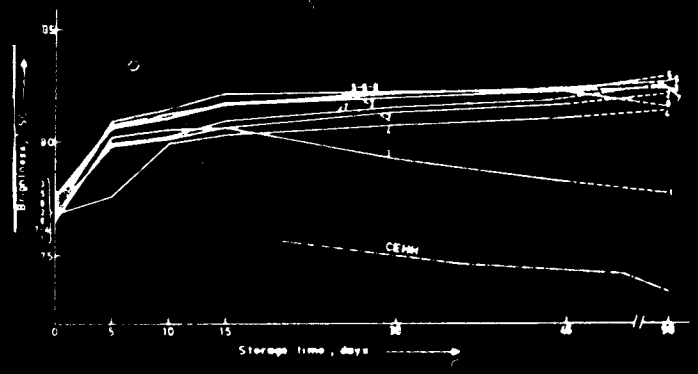
Reaction (II) involving the side chain



vanillyl type compounds — α-ketone (coloured compound) — α-carbonyl group oxidised

4 Peroxide spray bleaching of Bamboo kraft pulp after CEHH sequence (Brightness 78°ISO)

Brightness during storage time after flash drier



BLEACHING OF BAMBOO KRAFT PULP BY DIFFERENT SEQUENCES (CEHH CEHP CEHP

	Sequence		Chemicals, g/100 g o.d.p. Cl_2	NaClO, A.C.	NaOH	NH_4SO_4, M	H_2O_2	Temperature, °C	Duration, h	Final pH	Brightness, %ISO	Ageing: +24 h 105°C Brightness, %ISO	Ageing: +24 h 105°C P.C.	Ageing: 15 days 20–25°C Brightness, %ISO	Ageing: 15 days 20–25°C Drop, %ISO
		C	7.1					35	½	2.2					
		E			4.0			60	1½	11.7					
1	CEHH	H		3.0		0.12		40	2	7.7	76.8				
		H		1.5		0.06		60	2	8.0	80.6	61.2	10.04	77.9	2.9
2	CEHHP	Former CEHH sequence followed by													
		P			0.8		0.3	60	2	11.5	88.0	69.1	4.62	76.5	1.3
		C	7.1					35	½	2.2					
		E			4.0			60	1½	11.7					
3	$CEH_{1/2}P$	H		3.0		0.12		40	2	7.7	76.8				
		P			0.8		0.3	60	2	11.6	77.0	67.1	4.93	77.0	0.0
		C	7.1					35	1	2.2					
		E			4.0			60	1½	11.7					
4	$CEH_{1/2}E$	H		4.8		0.16		40	3½	7.0	80.5				
		P			0.8		0.3	60	2	11.2	82.5	69.2	4.43	78.7	0.8

NB Consistency: C = 3.5 %
E, H, P = 10 %

PEROXIDE BLEACHING IN THE FLASH DRIER OF BAMBOO KRAFT PULP AFTER CEHH SEQUENCE

(Brightness after CEHH : 78° ISO)

Brightness during storage time, °ISO

Trial	①	②	③	④	⑤	⑥	⑦	⑧	CEHH Reference
Chemicals, g/100 g									
H_2O_2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	
DTPA 40 %		0.1	0.1	0.1	0.1	0.1			
Silicate 38°Be			0.5						
$Na_2P_2O_7$				0.3		0.3	0.3		
Na_3PO_4					0.2	0.2		0.2	
H_2O_2 consumption after dryer	36 %	26 %	30 %	53 %	44 %	53 %	42 %	40 %	
Brightness after dryer	76.5	77.0	77.6	76.0	77.4	76.9	76.0	77.1	
after 5 days	80.2	79.8	80.7	77.6	80.6	80.7	78.9	80.9	
10 "	80.5	80.1	81.0	79.9	81.0	81.2	80.2	81.4	
15 "	80.6	80.6	81.6	80.3	81.7	81.6	80.9	82.1	
20 "	–	–	–	–	–	–	–	–	78.0
30 "	79.2	81.2	81.9	80.7	82.1	82.1	81.5	82.1	
35 "	–	–	–	–	–	–	–	–	76.6
45 "	78.2	81.6	82.2	81.0	82.3	82.2	81.8	82.2	
60 "	–	–	–	–	–	–	–	–	74.2
90 "	77.7	82.0	82.3	81.3	82.6	82.8	82.5	81.5	73.4
H_2O_2 consumption after Dry ageing after 15 days (105°C – 24 h)	100 %	100 %	89 %	74 %	83 %	74 %	74 %	100 %	
Co (ISO	71.3	70.4	70.5	69.4	71.0	71.0	70.4	71.8	
P.C.	3.46	3.99	4.10	4.33	3.87	3.84	3.97	3.66	

Bleaching of Bamboo kraft pulp by CEHH sequence

applied prior to spray bleaching

Sequence			Chemicals, g/100 g p Cl_2	NaClO, A.C.	NaOH	NH_4SO_4M		Temperature, °C	Duration, h	Consistency, %	Consumption, %	pH in.	pH fin.	Brightness, °ISO
			unbleached pulp – kappa = 35,7 →											22.3
C			7.14					35	½	3.5	99	1.7	1.7	–
	E	①			4.0			60	1½	10	–	12.0	11.0	–
		H		3.0		0.12		40	2	10	93	10.7	8.5	73.3
		H		1.5		0.06		60	2	10	45	11.0	9.0	78.0