

Soda-Formaldehyde as Pretreatment Agent for CottonWood ChemiMechanical Pulp

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ABSTRACT

Effect of soda and formaldehyde as pre-treatment chemicals during the chemimechanical pulping (CMP) of Populus deltoides have been studied. When the two chemicals are used in a mixture for cooking in one or two stages, the pulp has low strength properties, but when the chemicals are used in two separated stages the pulp become stronger although with lower brightness. For a same stage, increments in the formaldehyde quantities reduce the strength properties of the pulp but increase its birghtness; increments in temperature seem not affect significatively the breaking length, but the tear index is increased notoriously and the brightness and the light scattering coefficient are reduced considerably. By using a 4% hydrogen peroxide in two bleaching steps, a final brightness of 67.7% is obtained. With the use of formaldehyde during the obtention of CMP from cottonwood, considerably thermal brightness stability is observed, but only a low light stability.

INTRODUCTION

The manufacturing of mechanical pulp for papermaking is an attractive and efficient utilisation of wood resources. This high conversion of lignocellulosic material into mechanical paper insures minimal generation of waste products and improved environmental performance (Ragauskas and Cook, 1997). Interest is growing in expanding the use of high yield pulp as a component for the production of various grades of printing papers in addition to their current use in newsprint and magazine stock (Cole and Sarkanen, 1987). New grades of mechanical pulps, particularly bleached chemimechanical (BCMP) and chemithermomechanical pulp (BCTMP), are attractive candidates for replacing chemical pulps in different kind of papers (Johnson, 1989). The recent advances in these pulping processes and bleaching technologies have yielded CMP and CTMP with finalbrightness values in excess of 85% Tappi brightness, sufficient to permit their use as substitutes for chemical pulps in many grades of paper (Schmidt and Heitner 1991,

Heitner and Min, 1987). However, the loss of brightness that arises from exposure to light has left some uncertainties as to whether consumers will find these papers acceptable for some purposes. If it could be demonstrated that the light stability is adequate, papermakers could capitalise on the useful papermaking properties of this kind of pulps (Johnison, 1989). Inlight-induced ageing, reversion is dependent primarily on the wave length and intensity distribution of the light source and on exposure time. Ultraviolet wave lengths in the range of 300-370 nm are the most damaging, light of lower wavelength is not present in indoor lighting, while light of higher wave length can actually have a mild bleaching effect (Johnson, 1989).

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The core of the problem has been shown to be primarily attributable to the lignin component of the pulps (Leary 1968, Kringstadt 1969). In a later study (Lin and Kringstadt 1970), it was shown that the structural elements in lignin responsible for the initiation of colour-forming reactions, are ring-conjugated carbonyl and ethylenic groups and biphenyl structures.

In recognition of the proposed roles of ring-conjugated carbonyls and ethylenic groups, and phenolic hydroxyl groups in the yellowing of lignin on exposure to visible light, several studies have been undertaken, using the approach of chemically modifying the above structural elements as a means of photo-stabilising the lignin (Tschirner and Dence, 1988). Lin and Kringstadt (1970), found that the light stability of spruce lignin was considerably improved following reduction with borohydride, and when borohydride reduction was followed by catalytic hydrogenation, complete photostabilization was achieved. Acetylation not only improved the light stability of groundwood, but brightening of the pulp (Leary, 1968). A variety of alkylating agents was used by groundwood. Only propylene oxide, butylene oxide, dimethyl sulphate, benzoyl photostabilizing the pulp. Also a partial photostabilization of spruce lignin was reported, following diazomethane methylation (Gierer and Lin, 1972). The object of the present work was to determine the effect of soda formaldehyde as pre-treatment agents, during the obtention of CMP on the pulp characteristics and on the brightness stabilisation,

after bleaching with hydrogen peroxide and accelerated ageing.

EXPERIMENTAL

Cottonwood chips (*Populus deltoides*) with size between 3/4 and 1/2 inch, were impregnated during 24 hours, with soda, soda-formaldehyde and soda-sulphite. The cooks with liquor to wood ratio of 3.5 to 1 were carried out in two steps, using polyethylene bags and heated in a temperature controlled water bath.

In a first cooking series, the chemical used in the first cooking step was soda, and in the second step the chemical was formaldehyde according the table-1 the cooking temperature for both steps, was from 70°C to 150°C and the treatment time was 60 min. or 180 min.

A second cooking series were carried out according the table-2; the chemicals in the first cooking step were soda or a mixture of soda and formaldehyde, and in the second step only formaldehyde for some runs. The cooking temperature was 70°C and the treatment time 60 minutes.

The chips defibration was carried out always after the first cooking stage in a cooker-defibrator equipment, by 4 stainless steel plates, welded to a rotating shaft, and defibrating the chips against 4 fixed grooved stainless steel plates distributed in the inner wall of the cylindrical quiver. The defibering time was 60 seconds with a 30% consistency. After the second

Table-1 CMP cooking runs from cottonwood with soda and formaldehyde

1st cooking step (% soda)	2nd cooking step (% formaldehyde)	Cooking Temperature(°C)	Cooking time (min)	Breaking length (m)	Tear index (mNm ² /g)	Light absor. Coefficient (m ² /kg)	Light scatt. Coefficient (m ² /kg)	Brightness (% Elrepho)
7	0	90	180	1980	4.24	4.98	39.19	38.22
7	5	90	180	1900	4.03	4.77	40.21	38.80
7	10	90	180	1840	3.82	4.68	39.72	39.20
7	15	90	180	1795	3.59	4.60	38.22	39.50
7	20	90	180	1790	3.25	4.56	39.89	39.80
7	5	70	180	2102	5.70	3.33	41.19	44.30
7	5	70	60	2080	-	3.59	45.44	46.40
7	5	110	180	2110	6.02	9.60	36.00	32.70
7	5	130	180	2150	6.13	12.20	29.30	26.80
7	5	150	180	2219	6.23	14.03	21.15	22.70

24 hrs. Impregnation time, liquor to wood ratio 3.5/1, 60 °SR refining.

Table-2 CMP cottonwood cooking with soda, sulfite and formaldehyde.

1st cooking step (% soda + % sulfite)		2nd cooking step (% Formaldehyde)	Breaking length (m)	Tear index (mNm ² /g) (m ² /kg)	light absor. Coefficient (m ² /kg)	light scatt. Coefficient (m ² /kg)	Brightness (% Elrepho)
7	-	5	1547	3.65	3.16	41.03	48.74
7	-	-	1694	3.75	3.49	41.38	47.40
7	5	-	2036	4.18	2.24	39.40	48.34
7	5	5	2025	3.84	3.30	38.97	47.80

24 hrs. Impregnation time, liquor to wood ratio 3.5/1, cooking 70 °C, 60 minutes and 60 °SR refining.

cooking step, the pulp was refined in a Sprout Waldron 30-cm diameter disk refiner, using D2A 509 type disks and a 5% consistency and several loops refining until a 60 °SR were reached.

The screening of the refined pulp was carried out in a diaphragm cleaner with a 0.15-mm wide slotted screen over which the reject pulp was collected. The accepted pulp was recovered on a stainless steel mesh with 325 thread yarn/inch, with the object of drain the pulp and retain as much fines as possible. Some chosen pulps were bleached in two different series. In the first one with 9 runs, a 0.5% of DTPA pre-treatment was used as metallic ions inactivator at 5% consistency, room temperature and during 30 minutes; after that, the pulp was washed and squeezed. The bleaching were carried out in polyethylene bags with 10 gr. of pulp in a temperature controlled water bath.

The bleaching liquor was prepared with 0.15% magnesium sulphate, 4% sodium silicate, sodium hydroxide from 0.5 to 1.0% and 2% of hydrogen peroxide in each one of the two steps. The temperature and time for bleaching were 70°C and 120 minutes respectively for each step and 10% consistency. The bleaching conditions for the first bleaching series appear in table 3. The pulps from the second cooking series were bleached with 7 runs, using the same DTPA pre-treatment stated before and the same bleaching liquor, using fixed quantities of 1% soda.

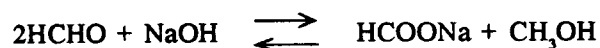
The paper sheets for the physical tests were made in an semiautomatic paper sheet former, model 255/SA, Testing Machines, Inc., using the T-205 TAPPI technique. The paper ageing was carried out by a thermic treatment in an oven at 105°C during 4 hr, and by a UV treatment in a photochemical reactor Rayonet Model RPR-100 with 16 2537 A UV lamps, with 35 Watts, an 1.65×10^{16} photons sec/cm³ intensity source. The paper samples were fixed in an 86 rpm rotating carousel, impelled by the wind of a cooling fan. The

distance from the paper and the UV lamps was 4 cm. The UV exposure time for the paper was one, two and three hrs.

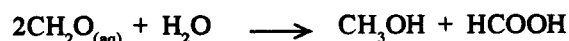
RESULTS AND DISCUSSION

YIELD

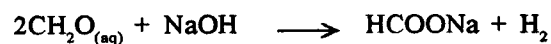
Normally the pulp yield is lower when in the first cooking steps only soda is used and in the second only formaldehyde, compared when a mixture of both is used in the two cooking steps. The combination of formaldehyde and soda counteract to each other as the formaldehyde is the simplest member of the aldehyde family and it is very reactive (Fisher 1992). For that reason there is a lower attack over the wood components. Even at room temperature, the formaldehyde can react with the sodium hydroxide at the moment; after heating, reaction proceeds according to the Canizzaro reaction (Zeng and Jiaying 1992).



Walker (1975), shows that the Canizzaro reaction involves the reduction of one formaldehyde molecule, with the oxidation of other:



Although the reaction is normally catalysed for alkalis, it also take place when the formaldehyde is heated in acidic medium. The reaction mechanism under alkaline conditions, involves hydrogen release, which reduces the formaldehyde to methanol:



The soda and the formaldehyde in separated steps attack in a stronger way the wood components and for this the yield is lower. If the cooking temperature and

STRENGTH PROPERTIES

Normally the mixture of soda and formaldehyde in one or two cooking steps, produce pulps with very poor strength properties, as much breaking length as

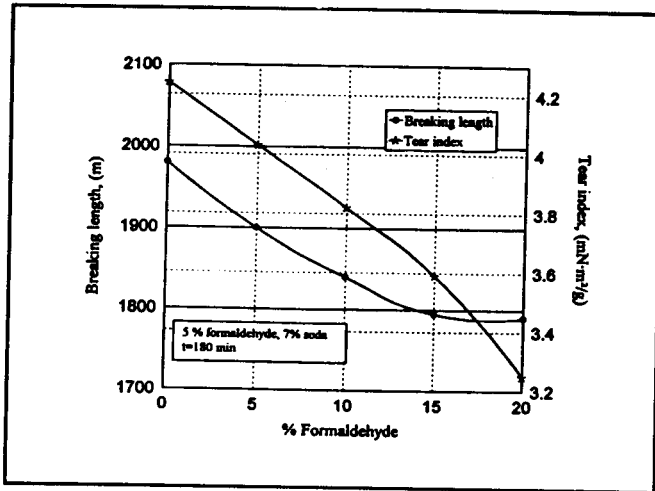


Fig. 1 The influence of formaldehyde over the breaking length and the tear index in the CMP from cottonwood.

time is kept constant at 90°C during 180 minutes and the soda is 7% in the first cooking step, the increments in formaldehyde in the second cooking step, reduce lightly the pulp yield. Also Zeng and Jiaying (1992), founded that the yield in CMP is reduced when the formaldehyde is increased in the pre-treatment.

Gardner and McGinnis (1988), also stated that the lignin can react with the formaldehyde to provide methylol functionalities, although they also point out that hardwood lignin's which contain a high percentage of syringyl units and highly condensed lignin have been shown to have limited reactivity with formaldehyde. Klashorst (1988), also point out that hardwood and softwood models compounds were hydroxymethylated on positions meta to the aromatic hydroxy groups, and the hydroxymethylation was achieved in high yield with a small excess of formaldehyde. In the same way, it has been shown that the formaldehyde reactions during the cooking in the CMP include hydroxymethylation in the lignin phenolic units (He et al, 1993). Also De Groote et al (1987) pointed out that an excess of formaldehyde in alkaline conditions, conduct to hydroxymethylation and polymerisation of lignin.

The increments in temperature reduce the pulp yield considerably and in minor proportion also the increments in treatment time. Also Zeng and Jiaying (1992) show that when the temperature is increased, the yield is reduced. Also according with them, with the addition of formaldehyde, the extractives, the lignin content, and the pentosans are reduced if the temperature is 100°C or higher.

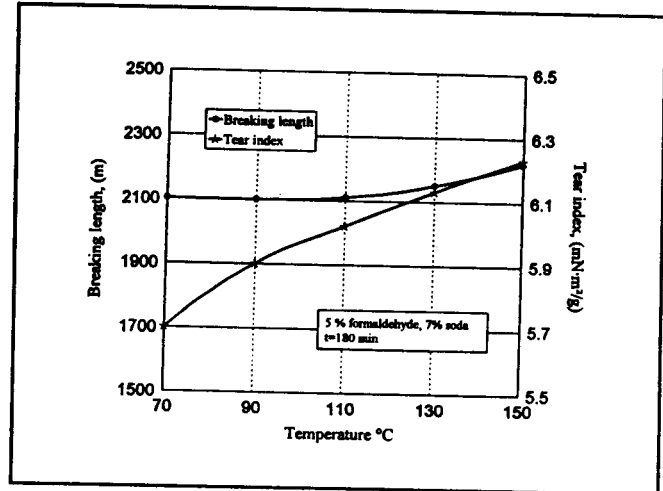


Fig. 2 The influence of cooking temperature over the tear index and breaking length of CMP.

tear. A continuous increment in formaldehyde in the second cooking step produces a continuous reduction in the pulp strengths (See table 1 and fig. 1). Also Zeng and Jiaying (1992) found a similar behavior, showing that under the same conditions the reduction in the pulp strength is produced for the formaldehyde addition. They pointed out that when the pulp is observed under the microscope, more broken fibres are found in the formaldehyde treated pulps as compared with the pulp from a process in which no formaldehyde is added. The increments in temperature seem not

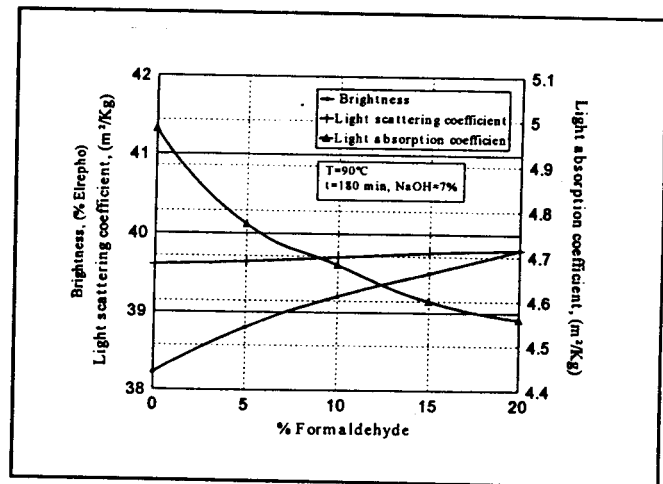


Fig. 3 The influence of formaldehyde over the brightness and the light absorption and scattering coefficients from cottonwood CMP

affect significantly the breaking length, but the tear index is increased notoriously, as can be observed in table 1 and fig. -2.

Comparing the strength properties from the pulp obtained with soda, soda-formaldehyde, soda-sulphite,

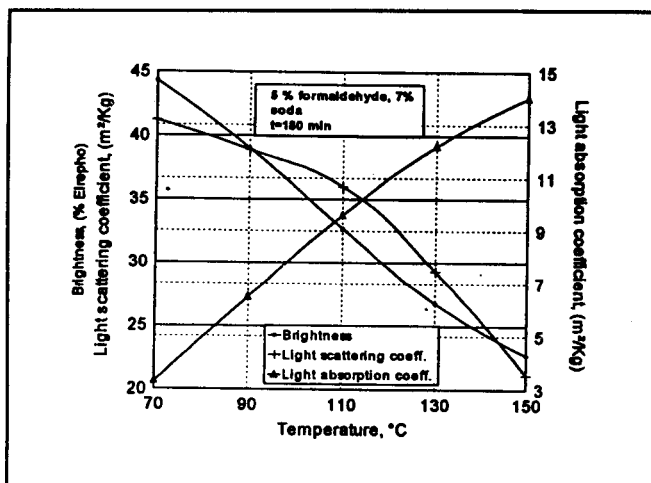


Fig. 4 The influence of cooking temperature over the brightness and the light absorption and scattering coefficients from cottonwood CMP.

and soda-sulphite-formaldehyde, the better properties are obtained with the combination of soda-sulphite and with soda-sulphite-formaldehyde (See table 2). Also Nakanon et al (1970), by using a combination of formaldehyde and sodium sulphite improved the pulp properties.

OPTICAL PROPERTIES OF THE UNBLEACHED PULP

The pulp brightness lightly increases with the continuous increments in formaldehyde quantities, rising from 38.2% Elrepho for no formaldehyde addition to 39.8% for a 20% formaldehyde (See table 1 and fig. 3). As a consequence, the light absorption coefficient is reduced from 4.98 m²/kg to 4.56 m²/kg with the same addition of formaldehyde. By other way, the formaldehyde seems not affect the light scattering coefficient.

By increasing the cooking temperature, the optical properties are considerably affected. The brightness with 44.3% value at 70°C is reduce to only 22.7% at 150°C, as is shown in table 1 and Fig. 4. In an opposite way, the light absorption coefficient is

Table-3 Bleaching conditions and optical properties of the cottonwood CMP obtained with soda-formaldehyde*

1st Treatment step	2nd Treatment step	3rd Treatment step	Final Brightness (% Elrepho)	Light absorption Coeff. (K _o) m²/kg	Light Scattering coeff. (S _o) m²/kg	Aged brightness (% Elrepho)	Aged light absorption Coeff. (K) m²/kg	P.C. n ⁽⁴⁾
2% H ₂ O ₂ ⁽¹⁾	2% H ₂ O ₂ ⁽¹⁾	-	65.80	0.52	48.10	65.70	0.66	0.29
2% H ₂ O ₂ ⁽²⁾	2% H ₂ O ₂ ⁽²⁾	-	65.10	0.52	50.20	65.20	0.64	0.24
2% H ₂ O ₂ ⁽³⁾	2% H ₂ O ₂ ⁽³⁾	-	62.70	0.59	51.31	62.80	0.75	0.31
2% H ₂ O ₂	2% H ₂ O ₂	5% Acetic Ac.	64.00	0.87	53.93	63.90	0.98	0.20
2% H ₂ O ₂	2% H ₂ O ₂	5% Formic Ac.	63.90	0.82	54.65	63.50	0.81	0.02
2% H ₂ O ₂	2% H ₂ O ₂	5% Formaldehyde	65.30	0.61	52.59	64.80	0.77	0.30
2% H ₂ O ₂	5% Acetic Ac.	2% H ₂ O ₂	65.80	0.52	51.16	65.80	0.60	0.16
2% H ₂ O ₂	5% Formic Ac.	2% H ₂ O ₂	65.70	0.48	50.59	65.80	0.58	0.20
2% H ₂ O ₂	5% Formaldehyde	2% H ₂ O ₂	66.60	0.48	51.08	66.10	0.63	0.29

* Obtained with 7% soda in the 1st step, 5% formaldehyde in the 2nd step, 70°C and 60 min.

The unbleached brightness, 46.4% Elrepho

(1) 1% Soda was used in bleaching step

(2) 0.75% Soda was used during bleaching

(3) 0.50% Soda was used during bleaching

(4) P.C. N^o = 100* ΔK/S_o

In all the other runs a 0.75% soda was used during bleaching

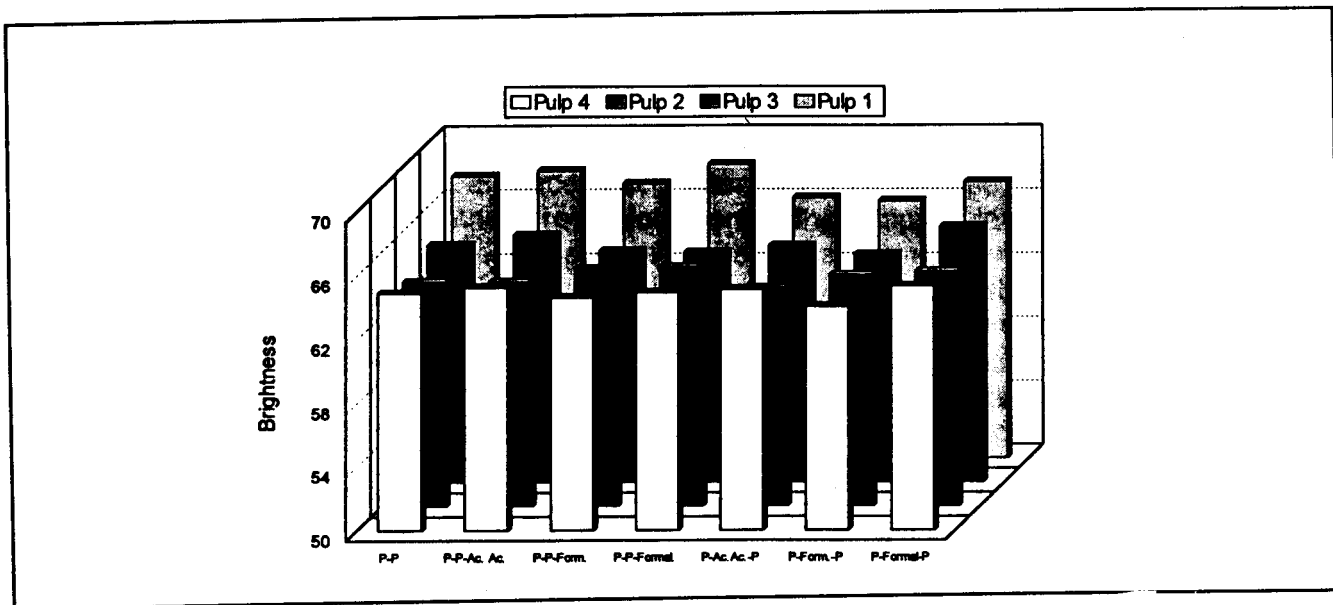


Fig. 5 Brightness from several cottonwood CMP, bleached with peroxide and other reagents.
NOTA: P=Peroxide (2%), Ac. Ac. = Acetic Acid (%), Form. = Formic Acid (5%) and Formal = Formaldehyde (5%)
Pulp 1 : 7% Soda-5% Formaldehyde, Pulp 2: 5% Soda, Pulp 3: 7% Soda + 5% Sulphite
Pulp 4: 7% Soda + 5% Sulfite - 5% Formaldehyde.

increased drastically with increments in temperature, from 3.33 m²/kg at 70°C, it is increased to 14.03 m²/kg at 150°C. By other way, the light scattering coefficient is reduced practically by a half between 70 and 150°C, reducing the value from 41.19m²/kg to only 21.15m²/kg.

Comparing the optical properties from the pulps obtained with soda, soda-formaldehyde, soda-sulphite and soda-sulphite-formaldehyde, there are not much differences in the brightness, but some lightly higher brightness are obtained with the combination of soda-formaldehyde and soda-sulphite (Table 2). The light absorption coefficient is also lightly lower for the some chemical combination. On the other hand, the light scattering coefficient is higher for the pulps cooked with soda or soda-formaldehyde.

OPTICAL PROPERTIES OF THE BLEACHED PULPS

With the use of 4% of hydrogen peroxide in two bleaching steps, the gain in brightness are from 14 to 19 points, increasing from 46.4% for the unbleached pulp to maximum value of 65.8% for the bleached pulp (Table 3). The increments in soda from 0.5% to 1% during the bleaching, increased the final brightness from 62.7 for a 0.5% soda to 65.1% for 0.75% soda and to 65.8% for 1% soda. The light scattering coefficient is higher when lower quantities of soda are

used during the bleaching, a similar behaviour is obtained for the light absorption coefficient. During the bleaching of the pulps, some treatments were made with formaldehyde after the two bleaching steps or in between; the final brightness was increased in 1.5 points, mainly when the formaldehyde treatment was made in between the bleaching steps. Also same treatments with acetic and formic acid between the bleaching steps, produce lightly increments in the final brightness of the pulp (Table 3). All the treatments with formaldehyde, acetic and formic acid, in both after the bleaching or in between the two bleaching steps, increase the light scattering coefficient from the pulps. The light absorption coefficient is reduced only when the treatments are between the two bleaching steps and only for the formaldehyde and the formic acid. The acetic acid treatment does not change the light absorption coefficient value (Table 3).

The pulp obtained only with soda reached a brightness gain of 16.7 points with 2% of hydrogen peroxide in each one of two bleaching steps, rising from 47.4% to 64.11%. If some formaldehyde treatment is made in between or after the bleaching steps, the final brightness in increased in one additional point. Also a treatment with formic acid increases lightly the brightness (fig. 5).

The pulp obtained with soda-sulphite reached a brightness gain of 16.5 points also with the 4%

hydrogen peroxide in two steps, from 48.3 to 64.9%. A treatment with 5% formaldehyde between the bleaching steps increases additionally the brightness in 1.1 points.

The pulp obtained with soda-sulphite-formaldehyde has a brightness gain of 17.1 points with 4% hydrogen peroxide in two steps, from 47.8 to 64.9% (fig. 5). A treatment with 5% formaldehyde when it is done between bleaching steps, seems to increase very lightly the brightness also a 5% acetic acid treatment after or in between the bleaching steps seems to improve lightly the brightness.

The pulp with the highest brightness is the one obtained with soda-formaldehyde in two steps, as the brightness gain after bleaching was 19 points, from 48.7% to 67.7%. The treatments with formaldehyde,

acetic and formic acids to not increase the brightness, showing similar values, and in some cases they seem to be lower than when no one treatment is done (Fig. 5).

BRIGHTNESS REVERSION

A considerable increase in the stability of the pulp can be achieved by introducing methoxyl, acetyl or benzoyl groups into the pulp. It has been proposed that the stabilisation is due to a replacement of free hydroxyl groups on the aromatic part of the lignin by these groups (Lorries 1968). It has been stated that the reactions of formaldehyde lead to some hydroxymethylation with phenolic moieties in lignin (He et al 1993, De Groote et al 1987). During this study the brightness loss after a thermal ageing was very low as we can see in table 3 by the brightness after ageing

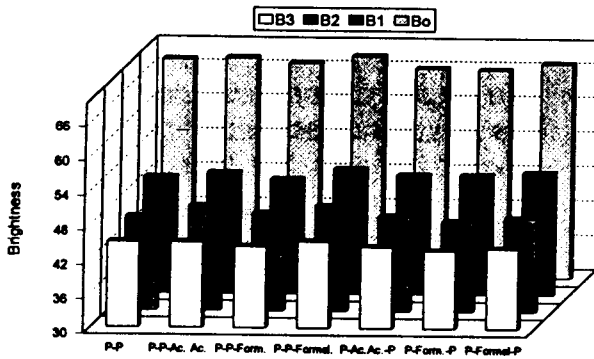


Fig.6 Brightness reversion after 1, 2 and 3 hours irradiation time in the cottonwood bleached CMP obtained with 7% soda-5% Formaldehyde.

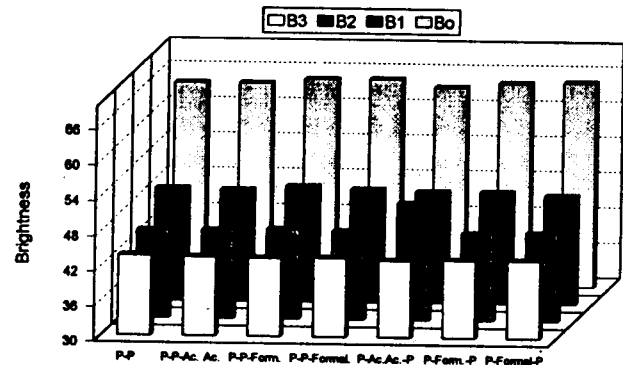


Fig.7 Brightness reversion after 1, 2 and 3 hours irradiation time in the cottonwood bleached CMP obtained with 7% soda.

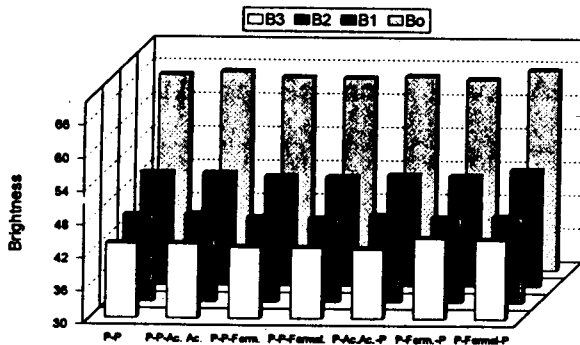


Fig.8 Brightness reversion after 1, 2 and 3 hours irradiation time in the cottonwood bleached CMP obtained with 7% soda-5% Sulfite.

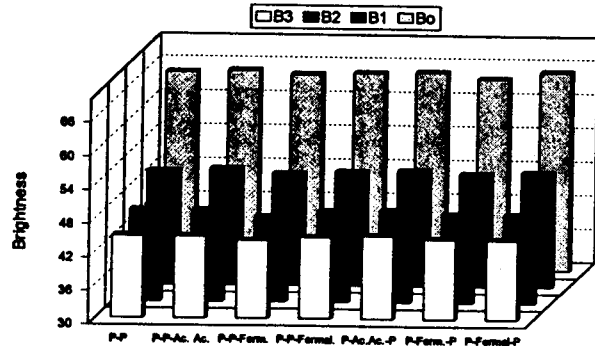


Fig.9 Brightness reversion after 1, 2 and 3 hours irradiation time in the cottonwood bleached CMP obtained with 7% soda+5% Sulfite-5% Formaldehyde.

NOTE: P= Peroxide, Ac.Ac.= Acetic Acid, Form.= Formic Acid and Formal= Formaldehyde. B= Brightness, Bo= initial Brightness, B1, B2, B3= Brightness after 1,2 and 3 hours irradiation time.

or by the post colour (P.C.) number (Giertz, 1945). The pulp before bleaching was obtained with 7% soda in the first step and 5% of formaldehyde in the second one. The use of formaldehyde, formic acid and acetic acid after, or in between the bleaching step seem not affect clearly the brightness reversion. Some other pulps obtained with soda, soda-sulphite, soda-formaldehyde and soda-sulphite-formaldehyde were light induced aged. The brightness reversion can be seen in figures 6, 7 8 and 9, where are represented different treatments of the pulp. The pulps 1 and 4, which have been produced using formaldehyde, presents lower average change in the light absorption coefficient Δk , lower P.C. number and higher brightness, after ageing for 3 hours with UV light even if all the brightness after ageing are lower than the unbleached brightness. The maximum quantity of chromophore formation is during the first hour of ageing, as can be seen in the P.C. values. The use of formaldehyde, formic acid and acetic acid after and in between bleaching steps, do not present a clear influence on the brightness stability (figures 6, 7, 8 and 9).

CONCLUSIONS

The uses of formaldehyde in a second stage during the CMP pulping increases the brightness of the pulp; however, the strength properties are reduced. For this reason only 5% formaldehyde is recommended with a temperature treatment as low as 70°C.

The best pulp properties are obtained when a combination of soda-sulphite and soda-sulphite-formaldehyde are used during the cooking, only for the light scattering coefficient, the pulps obtained with soda or soda-formaldehyde are lightly better.

The use of formaldehyde, acetic acid and formic acid after or in between the bleaching step, increase the final brightness and in some cases, also the light scattering coefficient. The highest brightness of 67.7% Elrepho is obtained when the pulp is produced with soda-formaldehyde in two steps.

The use of formaldehyde during the cooking of CMP from cottonwood imparts considerably thermal brightness stability, but only a low light stability is observed. The use of formaldehyde, formic and acetic acids after and in between the bleaching steps, do not present a clear influence on the brightness stability.

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REFERENCES

1. Cole, J.W.B. and Sarkanen, K.V.; TAPPI, 70 (11): 117 (1987).
2. De Groote R.A.M.C., Newmann G., Lechat J.R., Curvelo, A.S., and Alaburda J., Tappi J., p. 139, March 1987.
3. Fisher P.W., Environmental Conference Proceedings, p. 927, 1992.
4. Gardner, D.J., and McGinnis, G.D., Journal of wood chemistry and technology, 8(2)-261(1988).
5. Gierer, J.; and Lin, S.Y.; Svensk papperstidning, 75(7): 233(1972).
6. Giertz, H.W., Svensk papperstidning, 48(13)-317(1945).
7. He W., Tai D., and Lee Z., 7th International Symposium on Wood and Pulping Chemistry Proceedings, Vol. 1, p. 523, Beijing, May 25-28, 1993.
8. Heitner, C.; and Min, T.; Cellulose chem. and tech., 21(3):289(1987).
9. Johnson R.W., Tappi J., 72(12): 181(1989).
10. Klanshorst G., H.V., Journal of Wood Chemistry and technology, 8(2): 209 (1988).
11. Kringstad K.P., Tappi, 52(6)- 1070 (1969).
12. Leary, G.J., Tappi, 51(6): 257 (1968).
13. Lin, S.Y., and Kringstadt, K.P.; Tappi, 53(4): 658 (1970).
14. Loras V., Pulp and Paper Magazine of Canada, p. 57, January 1968.
15. Nakano J., Sumi Y., and Nagata M., Ippta, 7(1)-39 (1970).
16. Ragauskas and Cook, 9th Int. Symp. Wood and Pulping Chem., Montreal 1997, P. K6-1.
17. Schmidt, J.A.; and Heitner, C.: Journal of wood chem. and tech., 11(4): 397 (1991).
18. Singh, R.P.; Tappi, 53(9): 1675 (1970).
19. Tschirner, U.; and Dence, C.W., Paperi ja puu-paper and timber, 70(4): 338 (1988).
20. Walker J.F., Formaldehyde, 3rd Ed., Robert E. Krieger Publishing Co., New York, 1975.
21. Zeng Z. And Jiaying Ch., Second International Non-wood FIBRE Pulping and Papermaking Conference Proceedings, p. 214, April 6-9, Shangai, 1992.