

Photochemical Hydrogen Peroxide Bleaching of Eucalyptus Organosolv Pulp

Evandro A. Nascimento, Antônio E.H. Machado and Sérgio A.L. Morais

*Departamento de Química, Universidade Federal de Uberlândia,
38400-902 Uberlândia - MG, Brazil*

Lilian Borges Brasileiro and Dorila Piló-Veloso

*Departamento de Química, ICEx, Universidade Federal de Minas Gerais,
31270-901 Belo Horizonte - MG, Brazil*

Received: December 8, 1994; August 15, 1995

Avaliou-se uma alternativa para o branqueamento de polpas celulósicas baseada na utilização de peróxido de hidrogênio e radiação ultravioleta, em meio alcalino. A polpa celulósica foi obtida a partir de madeira de *Eucalyptus grandis*, empregando-se um processo de polpação organosolve. Nos ensaios, estudou-se a influência do pH do meio, da concentração de peróxido de hidrogênio e da temperatura sobre parâmetros relativos à qualidade da polpa. Os resultados mostraram que em um único estágio conduzido em pH 11, 0,47 M de peróxido de hidrogênio e temperatura de 35 °C, foi possível atingir 90% de deslignificação em apenas 1 h de reação, resultando uma polpa de boa viscosidade (20 cP) e alvura (60 °Elrepho). A concentração inicial de peróxido de hidrogênio foi substancialmente reduzida empregando-se silicato de sódio como agente estabilizante. A uma concentração de 12% em silicato de sódio e a 55 °C de temperatura, a concentração de peróxido foi reduzida a 15% (relativa à polpa seca). Esse procedimento permitiu obter uma polpa de melhor viscosidade (27 cP), embora o tempo de reação tenha aumentado para 210 min e a alvura tenha sido reduzida para 49 °Elrepho.

An alternative bleaching process for cellulose pulps using hydrogen peroxide and ultraviolet light in alkaline media was evaluated. Organosolv pulp from *Eucalyptus grandis* wood was used in the assays where the influence of pH, hydrogen peroxide concentration and temperature on the quality of the bleached pulp was studied in a one step process. At pH 11, 0.47 M hydrogen peroxide and 1 h of reaction at 35 °C, 90% of the delignification was obtained and a high viscosity bleached pulp resulted (20 cP). Under these conditions, a brightness of 60 °Elrepho was achieved. A drawback of this process is the high concentration of hydrogen peroxide which can, however, be greatly reduced by the addition of sodium silicate as a stabilizing agent. At a concentration of 12% sodium silicate (o. d. pulp) and at 55 °C, the peroxide concentration can be reduced to 15% (o. d. pulp). Although this improved pulp viscosity (27 cP), reaction time increased to 210 minutes and brightness decreased to 49 °Elrepho.

Keywords: *photochemical bleaching, hydrogen peroxide bleaching, eucalyptus organosolv pulp*

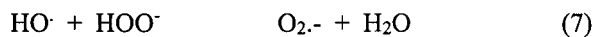
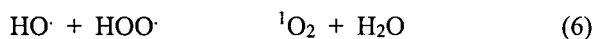
Introduction

Conventional bleaching processes present serious environmental problems due to the utilization of chlorine and

chlorine derivatives which can generate large amounts of chlorinated organic compounds. Therefore, because of stricter environmental laws, and a growing demand for chlorine free bleached pulps, many alternative bleaching

processes are being investigated, and great attention has been devoted to the use of chlorine dioxide, oxygen, peroxides and ozone.

Hydrogen peroxide is a strong oxidant which is largely used in the bleaching of high yield pulps, and also in chemical bleaching sequences¹. Its highest efficiency in bleaching and delignification is observed when the reaction is conducted in an alkaline medium. Under these conditions, the active species responsible for the elimination of chromophoric groups from lignin are perhydroxyl anions generated in hydrogen peroxide dissociation *via* an ionic pathway^{1,2}. On the other hand, radical species generated from the hydrogen peroxide alkaline decomposition are responsible for delignification processes^{3,4}. These radicals have an important role in the generation of secondary oxygen active species⁵⁻⁸ (Eqs. 1-8).



The possibility of the use of hydrogen peroxide in an alkaline medium as a source of oxygen active species in a process catalyzed by ultraviolet (UV) light, which enhances hydrogen peroxide decomposition and the production of hydroxyl radicals (HO^\cdot)⁵ has been recently demonstrated. Many other bleaching processes carried out in the presence of UV light using chlorine compounds⁹ and oxygen¹⁰ have already been studied. The satisfactory results obtained suggest the possibility of carrying out pulp bleaching experiments using hydrogen peroxide irradiated by UV light. These experiments present an alternative for the bleaching of cellulosic pulps.

Ionic and radical pathways usually take place during bleaching and delignification reactions. In order to obtain the greatest bleaching, both mechanisms must be combined, and the preponderance of one or the other depends on the conditions used¹¹.

Reactions involved in lignin oxidation by hydrogen peroxide in alkaline media are very complex and their mechanisms are not totally clear. However, two main types of reactions are considered: an electrophilic attack of molecular oxygen on carbanions (generated by the ionization of phenolic structures in alkaline media) and a nucleophilic addition of perhydroxyl anions to carbonyl structures. In

both cases there is strong evidence of hydroperoxide formation, although it has never been isolated. It is suggested that these hydroperoxides may react in many different ways, depending on their structures and the pH. Hydroperoxides may, for example, suffer an internal rearrangement resulting in the opening of aromatic rings and in the rupture of the $\text{C}_\beta\text{-C}_\gamma$ carbon bond of the propyl chain of α -keto structures¹². The formation of dicarboxylic acids has also been demonstrated¹³.

Radical species formed by hydrogen peroxide decomposition are also able to promote an electrophilic attack on lignin structures in the same way that molecular oxygen does^{4,14-16}. Some authors suggest that hydroxyl radicals are the main active species in the degradation and dissolution of lignin when hydrogen peroxide is irradiated by UV light¹⁷. Others have shown that the most active one is, in fact, singlet oxygen^{6,7,18}. Demethoxylation, hydroxylation and side chain oxidation of lignin structures are some of the reactions promoted by active radical species¹⁹.

During the bleaching process, part of the hydrogen peroxide is consumed in oxidation reactions, part decomposes to water and oxygen and another part remains unchanged in the bleaching liquor as residual peroxide²⁰. Hydrogen peroxide decomposition depends on several factors such as the pH of the medium, temperature and concentration of the impurities present in the pulp, reagents, water and the equipment used. The most significant effects are generally attributed to the formation of additional radical species, the generation of which is mainly due to the presence of transition metals²¹.

Hydrogen peroxide decomposition in alkaline media can be controlled by the addition of stabilizing agents, such as sodium silicate², magnesium salts²², and complexing agents like EDTA and DTPA^{23,24}. The selectivity of the bleaching process can be greatly enhanced by the use of sodium silicate, since the controlled decomposition of peroxide in radical species permits the degradation of the phenolic structures in lignin and avoids the extensive degradation of pulp carbohydrates^{1,4,14}.

Decisive parameters for obtaining good pulp properties are the pH of the suspension, the concentration of hydrogen peroxide, temperature and the use of stabilizing agents. These parameters were evaluated as a function of reaction time to determine the best conditions for a one-step bleaching process. Viscosity, mass loss, brightness and Kappa number were monitored during the process. The properties of the photochemically bleached pulps were compared with a chemically bleached one obtained from *E. grandis* wood.

Experimental

Eucalyptus grandis organosolv pulp (Kappa number = 63, 9.5% residual lignin; viscosity = 34 cP) was obtained

by the treatment of *E. grandis* wood with an ethyl acetate-acetic acid-water mixture²⁵.

For the bleaching assays, suspensions of the organosolv pulp (0.7% consistency) were prepared in distilled water and were irradiated by means of a refrigerated medium pressure mercury lamp (250 W, 220 V). Suspensions were maintained under stirring and were forced to circulate into a Pyrex glass spiral tube ($d_i = 1$ cm) set up around the lamp. Pyrex glass acted as a filter for the radiation, preventing the action of light of $\lambda < 320$ nm. The reactor used in the photochemical bleaching is shown in Fig. 1.

The use of UV irradiation in pulp bleaching is limited by the low efficiency of light penetration, although the active species generated in the decomposition of hydrogen peroxide suffer diffusion into the suspension. In order to increase the efficiency of the irradiation and to solve the problem of the small diameter of the reactor employed, the pulp consistency used was low in comparison to the consistency values reported in the literature. Recently, using another reactor geometry, a significant increase in pulp consistency was obtained²⁶.

Hydrogen peroxide in an alkaline medium was used as the bleaching agent. When the reactions were finished, the pulps were washed with a mixture of acetone-water (9:1), and then with distilled water. All reactions were carried out until no alteration in the color of the bleached pulps was observed.

A number of experiments were carried out involving changes in temperature, pH and hydrogen peroxide concentration²⁷⁻²⁹.

The selection of the best pH (pH = 11) for the process was made at 25 °C and a 0.62 M hydrogen peroxide concentration. The initial pH was obtained by the addition of diluted solutions of hydrochloric acid or sodium hydroxide. During the reactions, the pH was monitored with a Cole-Parmer mod. 5996-50 pH-meter.

The best hydrogen peroxide (0.47 M) concentration was estimated at 25 °C and pH 11. The best temperature was estimated using a 0.47 M hydrogen peroxide concentration at pH 11 (35 °C).

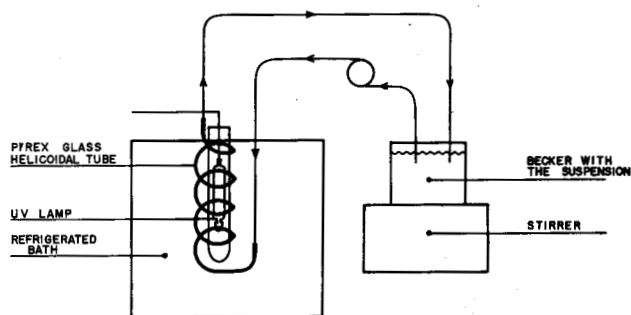


Figure 1. Scheme of the photobleaching reactor.

Sodium silicate was used in some experiments to control hydrogen peroxide decomposition and to reduce its concentration. The best sodium silicate concentration was determined in separate experiments in order to obtain the lowest Kappa number and the highest viscosity. Bleaching was conducted at 55 °C and with a hydrogen peroxide concentration of 15% (o. d. pulp).

The Kappa number (KN) was estimated by a procedure based on the Tappi Method T236 os-76, 1975. Klason lignin (KL) was evaluated from the approximate relation:

$$\% \text{KL} = \text{KN} \times 0.15$$

For bleached pulps a method described for a micro scale was employed³⁰.

Viscosity measurements were made with an electronic viscosimeter, Lab-Line Instruments, mod. ELV-8, 4537, according to a method based on the Tappi procedure T230 om-82, 1982. These measurements provided information about the degree of cellulose degradation.

Pulp brightness was determined at Laboratório de Celulose e Papel, Universidade Federal de Viçosa - MG, Brazil.

Results and Discussion

It was observed that the use of ultraviolet radiation does accelerate hydrogen peroxide organosolv pulp bleaching through the photochemical generation of radical species. This increases the reactivity of the system in terms of delignification, and also in terms of cellulose degradation. The results are discussed below.

The influence of pH

All parameters evaluated (Kappa number, viscosity, residence time, mass loss) were extremely dependent on pH (Table 1).

Figure 2 shows the dependence of viscosity on pH. As expected, in acidic media, an accentuated decrease in

Table 1. Organosolv bleached pulp properties as a function of initial pH (0.62 M H₂O₂; 25 °C).

pH	KN	Viscosity, cP	Mass loss, %	Reaction time, min
2.00	40.0	8.4	4.70	420
3.00	38.6	6.1	4.95	420
4.00	33.4	4.9	9.18	480
5.00	28.7	4.4	8.13	480
6.00	28.9	4.6	12.46	510
9.00	11.8	5.4	9.53	420
9.50	7.0	8.6	19.42	210
10.00	5.6	11.1	20.71	120
11.00	6.5	15.1	13.68	120
12.00	6.5	12.7	14.32	100

bleached pulp viscosity was observed because of the indiscriminate attack of hydroxyl radicals on cellulose fibers. Under these conditions, perhydroxyl ion formation from hydrogen peroxide dissociation was limited and the delignification rate was low. However, hydroxyl radicals were still being generated in the photochemical decomposition of hydrogen peroxide⁸, causing its low selectivity. Bleaching reaction time was also higher than that under alkaline pH. For reactions conducted at pH's below 6, bleaching was only partial, after 8 h, and the Kappa number reduction was about 50%.

For pH values ≥ 6 on, better results were obtained where the process becomes more selective and the ionic decomposition of hydrogen peroxide becomes dominant. Furthermore, in alkaline media, the ionization of the phenolic structures of lignin occurs, and this favors the electrophilic attack of oxygen and other radical species on this macromolecule. Confirming results reported in the literature³³, photochemical treatment in alkaline media is more effective than that in acidic media.

Bleaching reaction time presented a significant decrease above pH 10; about 90% of delignification was observed in less than 2 h of reaction. Consequently, pulp viscosity increased, with the optimum value being reached at pH 11. Under these conditions, a lower degradation of cellulose fibers combined with a significant decrease in the Kappa number can be observed.

The influence of hydrogen peroxide concentration

A decrease in the reaction time was observed with increasing peroxide concentrations, although no significant change was identified in the residual lignin concentration (Table 2).

A direct relationship between pulp viscosity and the initial hydrogen peroxide concentration was determined, as can be seen in Fig. 3.

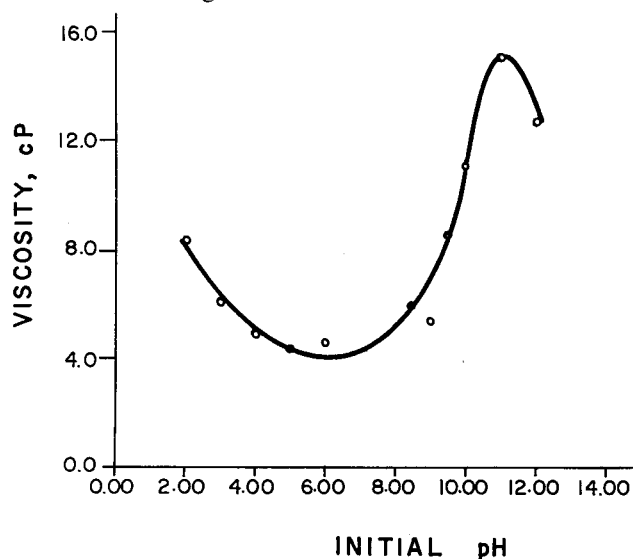


Figure 2. Bleached pulp viscosity as a function of pH.

Table 2. Organosolv bleached pulp properties as a function of the initial hydrogen peroxide concentration (pH 11; 25 °C).

[H ₂ O ₂], M	KN	Viscosity, cP	Mass loss, %	Reaction time, min
0.77	6.0	15.6	16.00	100
0.62	6.5	15.1	13.68	120
0.47	5.4	15.1	13.20	120
0.31	5.5	14.1	14.90	160
0.23	6.3	14.2	16.22	155
0.16	6.3	12.3	16.91	200

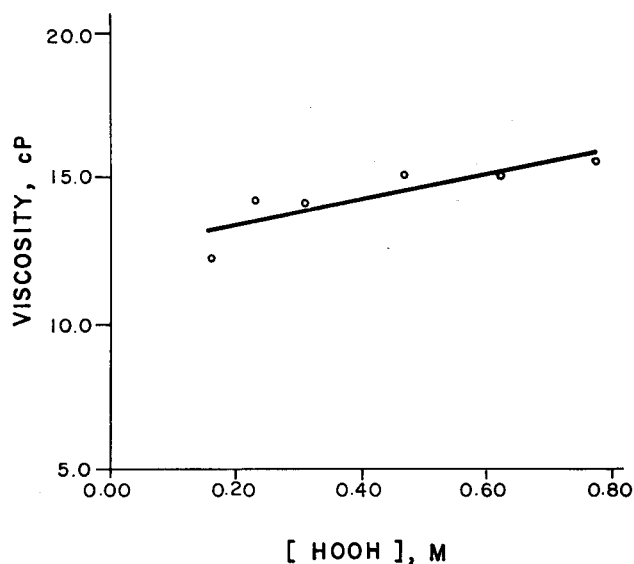


Figure 3. Bleached pulp viscosity as a function of the initial hydrogen peroxide concentration.

From Table 2 we can see that the residual lignin content remained practically the same, and so we can conclude that the reaction time was decisive for the increase in viscosity. The best results were obtained between 0.40 and 0.60 M of hydrogen peroxide. Lower concentrations resulted in higher losses of mass because of the longer amount of time exposed to UV light. In this case, carbohydrate degradation could be confirmed by the low viscosity obtained.

The initial hydrogen peroxide concentration of 0.47 M was chosen as the one which gave satisfactory bleaching results in terms of viscosity (15 cp), mass loss (13%), Kappa Number (5.4), and reaction time (2 h).

The influence of temperature

The effect of temperature was evaluated for reactions conducted at a 0.47 M hydrogen peroxide concentration and pH 11. Increasing temperature caused a considerable reduction in the reaction time (Table 3), due to the higher generation of active species promoted by hydrogen peroxide decomposition^{5,6}.

Table 3. Organosolv bleached pulp properties as a function of the reaction temperature (0.47 M H₂O₂; pH 11).

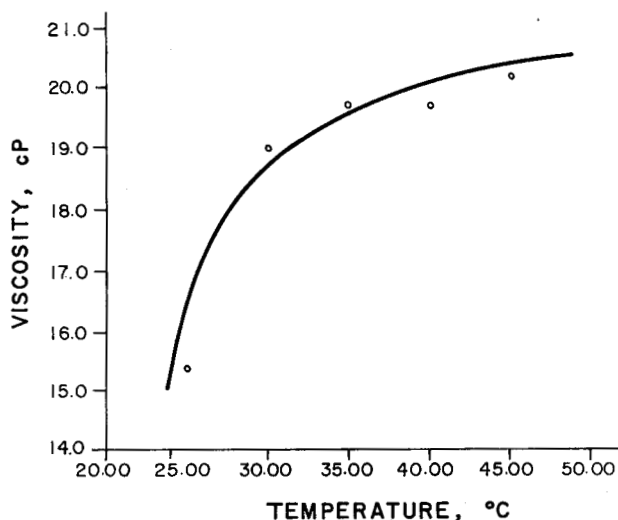
Temperature, °C	KN	Viscosity, cP	Brightness °Elrepho	Mass loss, %	Reaction time, min
25	5.4	15.4	64.9	13.25	150
30	5.8	19.0	57.6	13.92	75
35	7.3	19.7	60.7	16.23	60
40	6.8	19.7	-	20.19	50
45	7.5	20.2	65.9	19.02	45

A slight increase in the Kappa number was observed as the reaction temperatures of separate experiments were increased. Brightness, however, did not show behavior as regular as that of the other results previously obtained², in which the bleaching efficiency decreased with the increase in temperature.

An increase in temperature also caused an improvement in final pulp viscosity (Fig. 4). As the increase in viscosity was significant, it can be assumed that photochemical bleaching became more selective as the temperature was increased. This occurred because at reduced reaction times, the pulp contact with radical active species generated by the photochemical decomposition of hydrogen peroxide decreased.

We would expect a decrease in mass loss with an increase in the reaction temperature, since viscosity increased and residual lignin did not present a very significant change. To our surprise, mass loss increased with the temperature and this fact may be related to the preferential degradation of terminal groups of cellulose or to the removal of certain amounts of hemicelluloses without damage to pulp viscosity.

From these results, 35 °C was determined to be the best temperature for the photochemical bleaching under study.

**Figure 4.** Bleached pulp viscosity as a function of temperature.

Physical-mechanical assays

In order to make a comparison with a chemically bleached kraft pulp, the photochemically bleached organosolv pulp was submitted to physical-mechanical analysis. The results for the bleached kraft pulp, obtained from *E. grandis* wood with the same degree of refining as the organosolv one, were supplied by CENIBRA³². The results are presented in Table 4.

Traction or rupture length, deformation and explosion indexes of the photochemically bleached organosolv pulp are very similar to the indexes obtained for the chemically bleached kraft pulp.

The brightness value, however, was lower than that observed for the bleached kraft pulp. This fact represents the great limitation observed for a one-step bleaching based on hydrogen peroxide, and confirms the observations made by researchers studying non-photochemical processes using this reagent³³.

Table 4. Physical-mechanical analysis of bleached pulps.

Assay	Photochemically bleached	Chemically bleached
Base Weight	113.33 g/m ²	-
Thickness	0.16 mm	-
Porosity	10.66 s/100 cm ³	3.00 to 4.50 s / 100 cm ³
Traction	3800 m	4000 to 5000 m
Deformation	2.57 mm	2.00 to 3.00 mm
Explosion	2.73 Kg/cm ²	-
Explosion Index	2.36 kPam ² /g	2.30 to 2.70 kPam ² /g
Explosion Factor	24.08 gfm ² /cm ² g	-
Tear	48.0 gf	-
Tear Index	4.15 mNm ² /g	8.00 to 10.00 mNm ² /g
Tear Factor	42.35 100 gfm ² /g	-
Brightness	62.41%	91%
Opacity	98.0%	-

The porosity of the photochemically bleached pulp was relatively high, and its tear index, in contrast, was low when compared with the chemically bleached pulp. This weak property could be caused by the cellular wall thickness, which is greater than that expected for this wood (between 0.003 and 0.004).

The influence of sodium silicate

Although hydrogen peroxide photochemical bleaching presents good results in a laboratory, it would be not economically viable because of the very high concentration of the reagent used (0.47 M). A large part of the peroxide added would be consumed in the decomposition reactions, with damage to the cellulose fibers. So, the use of a stabilizing agent was investigated in order to reduce the reagent concentration and to improve the fiber properties.

In the presence of sodium silicate as a stabilizing agent, the hydrogen peroxide concentration usually employed for bleaching high yield pulps varies in the range of 2-4% (o. d. pulp)^{1,2}. In this work, this concentration was not enough to bleach the organosolv pulp due to its high lignin content and the low consistency of the suspension, which contributed to the dilution of the reagents. In this specific case, with the use of a stabilizing agent, the best hydrogen peroxide concentration determined was 15% (o. d. pulp).

The results obtained for different sodium silicate concentrations are shown in Table 5.

The residual lignin content, estimated as the Kappa number, decreased as sodium silicate concentration was increased. However, the brightness observed (49.0 °Elrepho) was less than that obtained in the absence of silicate (57.6 °Elrepho)²⁸.

The pulp viscosity was better than that observed in the absence of sodium silicate, confirming the stabilizing effect on hydrogen peroxide decomposition and lower degradation of cellulose.

An increase in mass loss was observed as sodium silicate concentration increased. At first glance, we thought that this fact was not significant because the delignification degree was not the same for all tests. However, the increase in mass loss was higher than the reduction in lignin content, indicating that different delignification degrees do not mask these losses. Although we are not sure, the losses of

Table 5. Organosolv bleached pulp properties as a function of sodium silicate concentration (15% H₂O₂; 15% NaOH; 0.8% EDTA; 55 °C).

% Na ₂ SiO ₃	KN	Viscosity, cP	Mass loss, %	Reaction time, min
4	14.0	24	10.46	210
8	12.0	23	11.35	180
12	9.7	27	14.45	210
15	9.7	27	15.32	180

mass could have been caused by the preferential degradation of terminal groups of cellulose or by the removal of certain amounts of hemicellulose.

The best sodium silicate concentration for alkaline hydrogen peroxide photochemical bleaching was 12%, under the conditions employed.

Conclusions

Hydrogen peroxide together with UV light in alkaline solutions accelerates pulp delignification. The high number of oxygen active species present in this process is implied in an indistinct route for lignin degradation.

This one-step bleaching process permits pulps of a relatively good quality to be obtained, working at low temperatures and reduced times.

The best pH for the photochemical hydrogen peroxide bleaching of the eucalyptus organosolv pulp was 11. At this pH and 0.47 M hydrogen peroxide it is possible to reach approximately 90% delignification, maintaining good pulp viscosity (around 20 cP) and a brightness level of 60 °Elrepho. Physical-mechanical results for the bleached pulp were also relatively good, considering that the process was carried out at 35 °C, for just one hour of reaction.

Hydrogen peroxide concentration could be significantly reduced by the use of sodium silicate as a stabilizing agent. With 12% sodium silicate and a higher temperature (55 °C), the peroxide concentration was reduced to 15% (o. d. pulp). This significantly improved pulp viscosity, reducing the peroxide attack on pulp fibers, but the reaction time increased and delignification suffered a small reduction. Brightness also decreased to 49 °Elrepho.

References

1. D. Lachenal, C. Choudens and P. Monzie, *Tappi* **63(4)**, 119 (1980).
2. J.L. Colodette, M.G. Fairbank and P. Whiting, *J. Pulp Pap. Sci.* **16(2)**, 53 (1990).
3. J.H. Roberts Jr., M.M. Morrison and D.T. Sawyer, *J. Am. Chem. Soc.* **100(1)**, 329 (1978).
4. R. Agnemo and G. Gellerstedt, *Acta Chem. Scand.* **B33**, 337 (1979).
5. A.E.H. Machado, PhD Thesis (Universidade de São Paulo - IFQSC, São Carlos, Brazil, 1991).
6. A.E.H. Machado, R. Ruggiero and M.G. Neumann, *Química Nova* **17**, 111 (1994).
7. A.E.H. Machado, R. Ruggiero and M.G. Neumann, *J. Photochem. Photobiol.* **A81**, 107 (1994).
8. K. Tatsumi and N. Terashima, *Mokuzai Gakkaishi* **31**, 761 (1985).
9. L.D. Markhan and S.K. Vidyarthi, *Tappi* **60(9)**, 138 (1977).
10. B. Marcoccia, D.A.I. Goring and D.W. Reeve, *J. Pulp Pap. Sci.* **17(2)**, 334 (1991).

11. S. Omori and D.W. Dence, *Wood Sci. Technol.* **15**, 67 (1981).
12. J. Gierer and F. Imsgard, *Sven. Papperstid.* **16**, 510 (1977).
13. G. Gellerstedt, H.-L. Hardell and E.-L. Lindfors, *Acta Chem.Scand.* **B34(9)**, 669 (1980).
14. J. Gierer, *Holzforschung* **36**, 55 (1982).
15. D.W. Sundstron, B.A.Weir and H.E. Klei, *Environ. Progress* **8(1)**, 6 (1989).
16. K. Tatsumi and N. Terashima, *Mokuzai Gakkaishi* **30(7)**, 580 (1984).
17. K. Tatsumi and N. Terashima, *Mokuzai Gakkaishi* **29**, 530 (1983).
18. R. Ruggiero and A.E.H. Machado, *XV IUPAC Symposium on Photochemistry* (Prague, Czech Republic, 1994), p.144.
19. E. Yang, J. Gierer and R. Torbjorn, *Proceedings of the Second European Workshop on Lignocellulosics and Pulp* (Grenoble, France, 1992), p.169.
20. J.L. Colodette and C.W. Dence, *J. Pulp Pap. Sci.* **15(3)**, J79 (1989).
21. P.K. Smith and T.J. McDonough, *Sven. Papperstidn.* **12**, R106 (1985).
22. J. Abbot and G.B. Douglas, *Appita* **43(6)**, 415 (1990).
23. J. Abbot, *J. Pulp Pap. Sci.* **17(1)**, J10 (1991).
24. T. Ali, D. McArthur, D. Stott, M. Fairbank and P. Whiting, *J. Pulp Pap. Sci.* **12(6)**, p. J166 (1986).
25. M.G.T. Hernández, PhD Thesis (Universidade Federal de Minas Gerais - ICEX, Belo Horizonte, Brazil, 1993).
26. A.E.H. Machado, R. Ruggiero, G.H. Terrones, A. Nourmamo, S. Grelier and A. Castellan, *J. Photochem. Photobiol.* submitted.
27. L.B. Brasileiro, Master's. Thesis: Universidade Federal de Minas Gerais, Belo Horizonte, Brasil, 1993.
28. L.B. Brasileiro, D.P. Veloso, E.A. Nascimento, A.E.H. Machado and S.A.L. Morais, *Proc. Second Europea Workshop on Lignocellulosics and Pulp* (Grenoble, France, 1992), p.193.
29. L.B. Brasileiro, D.P. Veloso, E.A. Nascimento, A.E.H. Machado and S.A.L. Morais, *Proc. Third Brazilia Symposium on the Chemistry of Lignins and Other Wood Components* (Universidade Federal de Minas Gerais, Belo Horizonte, Brazil, 1993), IV, p. 224 and 239.
30. V. Berzins, *Pulp Pap. Mag. Can.* **4**, T206 (1966).
31. R.H. Turner, U. S. Pat. Number 4292654 (1981).
32. CENIBRA - Celulose Nipo-Brasileira, Minas Gerais, Brazil.
33. D. Lachenal, C. Chirat and M.T. Viardin, *Proc. Second European Workshop on Lignocellulosics and Pulp* (Grenoble, France, 1992), p.89.