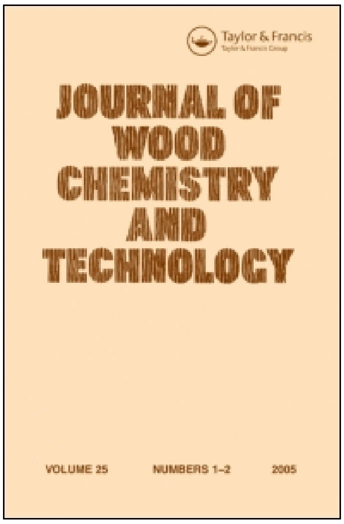

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Sylvain Robert[a]; Jean-Patrice Lamothe[a]; Claude Daneault[a]
[a] Centre de Recherche en Ptes et Papiers, Université du Québec à Trois-Rivières, Trois-Rivières, Québec, Canada

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BRIGHTNESS OPTIMIZATION OF OZONE PRE-TREATMENT FOLLOWED BY PEROXIDE BLEACHING OF TMP PULP FROM TAMARACK (*Larix laricina*)

Sylvain Robert §, Jean-Patrice Lamothe and Claude Daneault

Centre de Recherche en Pâtes et Papiers, Université du Québec à Trois-Rivières
P.O.Box 500, Trois-Rivières, Québec, Canada, G9A 5H7

§ To whom correspondence should be addressed

ABSTRACT

This study examines the influence of ozone on a TMP pulp of tamarack in an independent bleaching stage and as a pre-treatment for hydrogen peroxide bleaching. Ozone charges of up to 6% were used on dry pulp. The results were compared to those obtained with 1% H_2O_2 bleaching. Experiments were conducted at 23°C and 55°C, and pH varied from 3.5 to 10.5. The best bleaching results were reached with acidic pH, with interesting behavior observed at an alkaline pH level. Ozone effectively attacks CO groups in lignin, but lacks the chemical selectivity and high reactivity required to become a good bleaching agent.

INTRODUCTION

During recent years, the technological developments for refiners have improved mechanical pulp quality, particularly since the appearance of thermomechanical (TMP) and chemithermomechanical (CTMP) pulps. These pulps have become much cheaper to produce, i.e. about one fifth the cost of Kraft pulps [1]. The main goal in making these pulps is to take a share of the market of long-life fine papers already held by chemical (CMP) pulps. Unfortunately, the major drawback of TMP and CTMP pulps is their brightness and color reversion observed upon irradiation by sunlight. As long as this problem remains unresolved, TMP and CTMP pulps will not compete successfully except with newspaper grade pulps. This is unfortunate because TMP and CTMP pulps could use less popular wood species [2]. In addition, the processing of these pulps does not require chlorine. As a result, no dioxin is produced. Their paper properties, e.g. bulk, opacity and power of absorption, make them ideal pulps for absorbing tissues, cardboard, writing paper and impression paper [1].

It is thus important to pursue research on new ways to obtain a high level of brightness and to reduce brightness reversion. This is why we are working on new processes to produce high bleached pulps from unused wood species. Two classes of chemical reactions are involved in bleaching pulp, by oxidation or by reduction of the various chromophores encountered on the pulp and located on the lignin macromolecule. Hydrogen peroxide (H_2O_2) and oxygen (O_2) are currently used as oxidative bleaching agents in the pulp and paper industry and both provide excellent results. But there exist a stronger oxidizer which is encountered as an allotropic form of the latter, namely ozone (O_3). Only fluorine (F_2) and atomic oxygen exhibit a stronger oxidative potential than ozone. Because ozone is a non-specific chemical reagent, this powerful oxidizer also strongly reacts with aliphatic and aromatic carbon-carbon double bond (see Figures 1 and 2 [3]). These carbon-carbon double bonds, along with phenol and carboxy groups, are the precursors of the radical formation that takes place in lignin upon irradiation by ultraviolet light under an oxygen atmosphere [4,5,6], These reactions lead to the formation of quinoid [7,8] and polycyclic structures [9,10,11] which absorb light in the visible portion of the electromagnetic spectrum, giving its distinctive yellowish tint to the pulp.

Since ozone is such a powerful oxidizer, and since it reacts strongly with unsaturated structures, we attempted to use it as a pre-treatment for hydrogen peroxide bleaching, or as a stand-alone bleaching stage. In this paper, we will try to answer some of the following questions: Is it possible to carry out ozonization at the same temperature as the one used for hydrogen peroxide bleaching, or can we use a lower one? Which ozone charge should be applied at this temperature? Can an

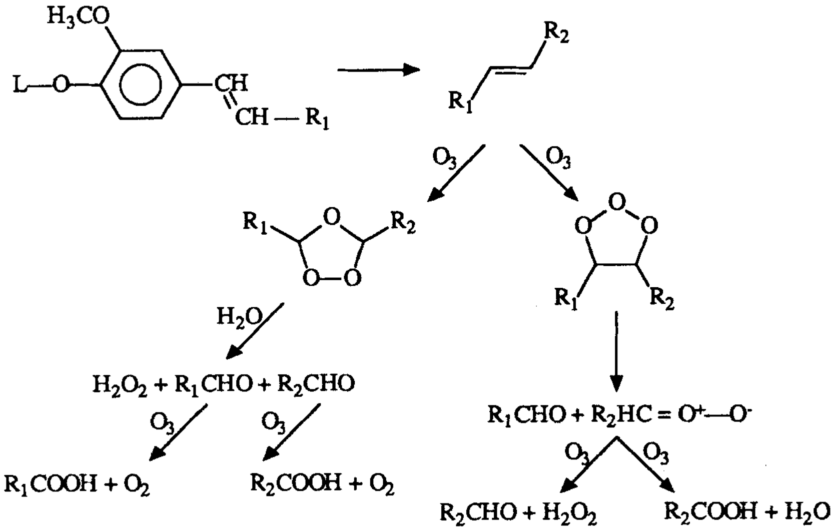

Figure 1. Chemical reactions of ozone with aliphatic carbon-carbon double bonds.

ozone treatment be used at high alkalinity (pH=10.5) as in the case of hydrogen peroxide, or must we use a more acidic pH? Since the reaction mechanism of ozone is radical, pH is not supposed to influence the reaction mechanism, but since high pH favors the swelling of fibers, and the action of ozone is a surface phenomenon, we can expect better ozone absorption at high pH.

We have studied the effect of temperature, pH and ozone charge on the optical properties of a tamarack thermomechanical (TMP) pulp subject to gas phase ozonization. Lindholm [12,13,14] showed that liquid phase ozonization at 0.1% to 3.0% pulp consistency allows consumption of about 60% to 80 % of the ozone. On the other hand, Lindholm [12] also demonstrated that it is possible to use up to 90% of the ozone if ozonization is carried out at high pulp consistency, 25% to 60%, in a gaseous phase. According to his work, ozonization at high consistency yields pulps with better mechanical properties. Secrist and Singh [15] reported that optimum O_3 consumption occurs somewhere between 40% and 60% pulp consistency. A 40% consistency level is easily obtained through pressing, and the laboratory equipment for ozonization is relatively simple.

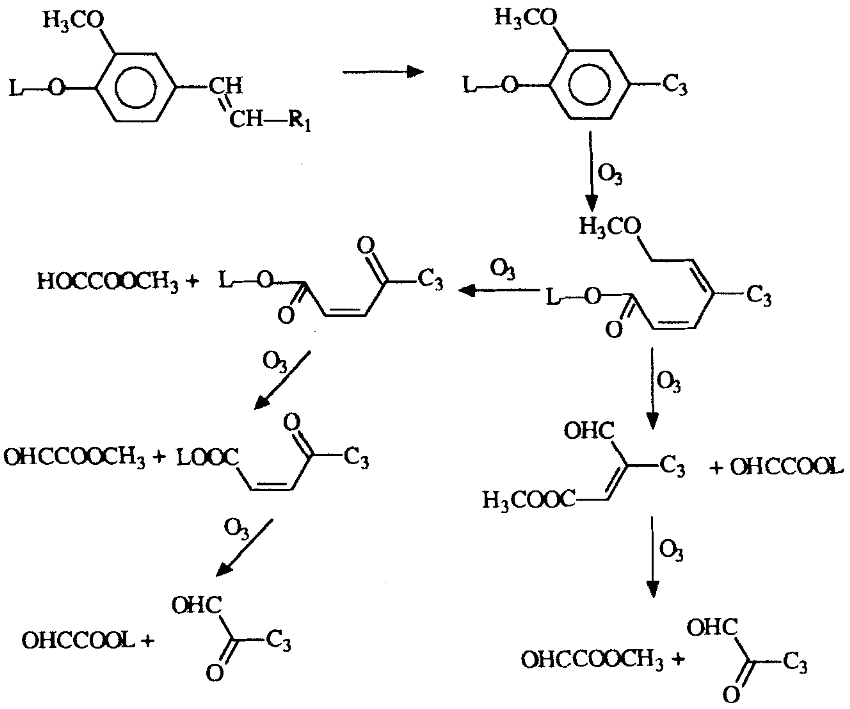

Figure 2. Chemical reactions of ozone with aromatic carbon-carbon double bonds.

MATERIALS AND METHODS

A thermomechanical pulp of tamarack (*Larix laricina*) was used. Tamarack is an untraditional softwood species sometimes used in Europe and the USSR in the production of sulfite and Kraft pulps [16,17]. Some recent studies have demonstrated its potential as a high-yield TMP pulp [18].

The wood used for this work came from St-Édouard, a natural forest in the Province of Québec, and is about 35 years old. It was chipped and classified with a Rader model M-2215 classifier. The chips which were accepted were less than 8 mm thick and had a bark content of about 6%. The TMP pulp was prepared according to the following procedure. Chips were washed and then steamed for 10 minutes at atmospheric pressure. They were cooked for 5 minutes at 125°C and refined first at 260 kPa (2.57 atm), and then at atmospheric pressure. The pulp thus obtained had a freeness of 120 mL. Its mechanical properties were acceptable, except for its brightness, measured 30% and 35% ISO.

The pulp was treated with DTPA to produce complexes with undesirable heavy metal ions in the form of a chelate molecule. This treatment was undertaken at 3% pulp consistency at room temperature for 15 minutes. DTPA was added at 0.5% (w/v) on dry pulp. The pulp was thickened to a 25% consistency level and stored in the dark in sealed polyethylene bags at 4°C until the experiment took place. A pulp sample which was not treated with DTPA was kept to serve as a reference to monitor the influence of DTPA on ozonization.

We also studied the effect of pH on ozonization, with pH values equally distributed around neutrality, namely 3.5 - 6.0 - 8.0 and 10.5. To fix the pH, the pulp was diluted to a 3% consistency level and the pH was adjusted with small additions of hydrochloric acid or sodium hydroxide. The mixture rested for 1 hour to allow the pH to stabilize. The pulp was then drained to a 25% consistency level and processed in a fluffer, where consistency level was brought to a value above 40%. The equivalent of 20 g dry pulp was then put in opaque polyethylene bags, in which the necessary water was added to obtain the fixed consistency level of 40%. The bags were sealed and left at room temperature for 24 hours to allow uniform humidity of the pulp. The samples prepared as described above were then used within 24 hours. There was thus a maximum delay of 72 hours between the moment pulp was made out of chips to its use in ozonization reactions.

The ozone which was used in the study was produced by an ozonizer from Ozone Research and Equipment Corporation (OREC, model 03B4-0, Testing Machine International, Montréal, Québec). It has a maximum output of 72 g $O_3 \cdot h^{-1}$. Gas-phase ozonization was carry out in the following way. The pulp was placed in a 2000 mL glass flask fixed to a modified rotary evaporator (Büchi, Rotavapor model M, Brinkmann Instruments Co., Rexdale, Ontario) and lowered into a thermostatic bath, as shown in Figure 3. This setup was used before successfully

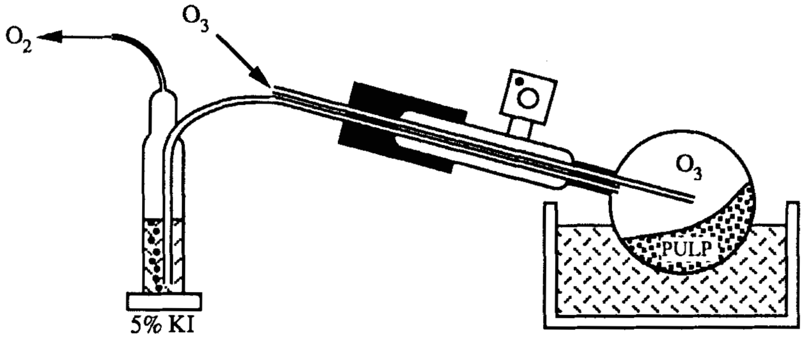

Figure 3. Experimental setup used to carry out gas phase ozonization.

[19] and is based on the one described by Liebergott [20] for the Paprizone process. It allowed the ozone and the pulp to be well mixed and increased the possibilities for chemical reactions on the surface of the pulp. Heidt and Landi [21] demonstrated that ozone is relatively unstable with self-oxidation as alkalinity increases to pH=10, with a half-life period of about 2 minutes. But you should note that these experiments were carried out in aqueous solutions. Considering this, care must be taken to overcome this problem. Liebergott [20] showed, with the Paprizone process, that if ozonization is carried out at a pulp consistency level of 30% to 40%, a considerable part of the ozone is immediately consumed, thus overcoming the risks of ozone auto-oxidation. The reason is simple, a 40% consistency level being very far from an aqueous solution. This design allows very good gas-pulp contact. In our setup, ozone was introduced in a flask via a special Teflon® fitting (Jonston Plastic, Ville La Salle, Québec) to ensure that no side chemical reactions with metal could occur. The resulting setup produced pulp that was free of patches, since bleaching had occurred evenly on the surface of the pulp.

After reaction with the pulp, excess ozone was bubbled through a 5% (w/v) solution of potassium iodide. The excess of ozone was measured by a iodometric titration with a 0.1 N solution of sodium thiosulfate as follows:

$$O_3 + 2\ KI + H_2O \rightarrow O_2 + I_2 + 2\ KOH$$

$$I_2 + 2\ Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2\ NaI$$

The average ozone input rate was measured at about 40 $mg \cdot min^{-1}$. Ozone charges were 0.0 - 2.0 - 4.0 and 6.0% (w/w dry pulp). The temperature of the ozonization bath was either 23°C or 55°C.

These conditions were used as a stand alone bleaching stage and as pre-treatment for hydrogen peroxide bleaching. When hydrogen peroxide is involved as a bleaching agent, the following procedure is used: magnesium sulfate ($MgSO_4$, 0.05% w/v), sodium silicate (Na_2SiO_3, 0.5% w/v), sodium hydroxide (NaOH, 3.0% w/v) and finally hydrogen peroxide (H_2O_2, 1.0% w/v) are added, in that order, to 20 g of dry pulp in a polyethylene bag. Pulp consistency level was adjusted to 15%, and the whole was triturated in an homogeneous mixture. The initial pH was somewhere between 10.5 and 11.5. The bag was sealed and placed in a thermostatic bath, at either 23° or 55° C. A 10 minute delay was needed to achieve thermal equilibrium of the mixture. Then the bleaching was processed for 120 minutes at 60°C. The mixture was mold at regular intervals to ensure homogeneity. After bleaching, the final pH was 9.5 or more. The pulp was then thoroughly washed with distilled water and the pulp, at a 1% consistency level, was neutralized with sodium pyrosulfite ($Na_2S_2O_5$, 1% w/v) for 5 minutes.

The pulp content in carboxylic acid groups was measured by titration with sodium hydroxide after the experiments took place. Standard sheets for optical tests were prepared according to CPPA Standard Method C.5. Optical properties were measured on a photoelectric reflectance photometer (Carl Zeiss, model ELREPHO, Oberkochen/ Wuertt, West Germany) according to CPPA Standard Method E.1 and E.2.

RESULTS AND DISCUSSION

All the results on the present study appear in Table 1 which also served as a basis to build the various bar graphs shown in the remaining of the paper. The table

TABLE 1

ISO brightness (%) and COOH content (mmol•kg^{-1}) of pulp for varying pH, temperature and bleaching conditions.

pH =	3.5	6.0	6.0	8.0	10.5	10.5
T (°C) =	23.0	23.0	55.0	23.0	23.0	55.0
O_3 charge (%)	ISO Brightness for O_3 only					
0	32.5	31.6	31.6	32.1	28.7	28.7
2	34.8	33.6	34.3	34.9	31.9	31.3
4	35.7	34.6	35.5	35.7	34.0	33.5
6	36.0	35.3	35.6	35.9	35.1	34.8
	ISO Brightness for O_3 + 1% H_2O_2					
0	35.5	34.9	34.9	35.1	34.2	34.5
2	35.9	35.4	35.7	35.7	34.8	35.4
4	36.2	36.1	36.5	36.4	35.1	35.6
6	36.5	37.0	37.2	37.1	35.3	35.6
	COOH content for O_3 only					
0	157	152	154	151	152	162
2	204	186	186	187	188	188
4	228	207	222	220	214	220
6	241	226	236	237	229	240
	COOH content for O_3 + 1% H_2O_2					
0	226	205	209	223	220	218
2	253	219	223	244	228	235
4	268	224	232	256	233	248
6	279	234	240	268	240	255

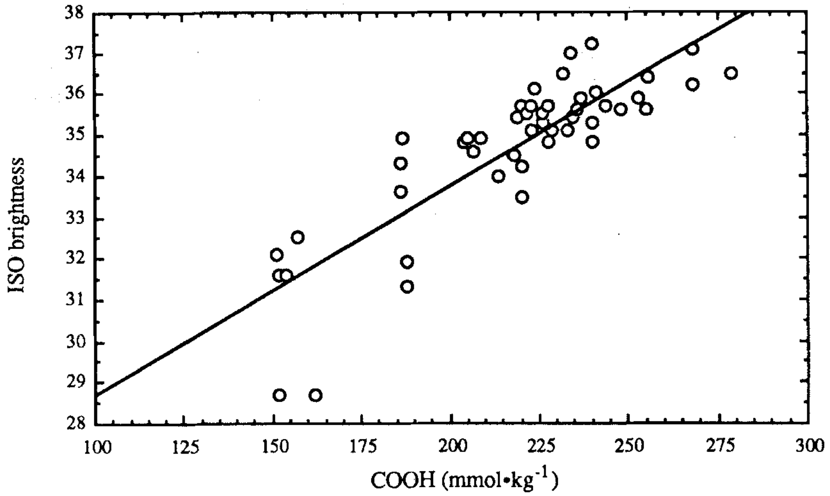

Figure 4. Relation between ISO brightness and the carboxylic acid content of the pulps. All our results are shown. Some experiments were carried out at 23°C with a pH of 3.5 – 6.0 – 8.0 and 10.5. Others were done under the same conditions followed by 1% hydrogen peroxide bleaching. Some experiments were submitted to a temperature of 55°C with a pH of 6.0 and 10.5, while others still were carried out under the same latter conditions followed by 1% hydrogen peroxide bleaching.

shows the values of ISO brightness (%) and COOH content (mmol•kg^{-1}) for ozone only (first and third set of data) and ozone-peroxide (second and fourth set) bleaching. The conditions are expressed as a function of pH and temperature. The pH was varied from 3.5 to 10.5 from left to right. Experiments at 23°C and 55°C are also shown. As shown in Figure 4, the carboxylic acid content of the pulps appears to be directly proportional to ISO brightness, e.g. for a sheet made from ozonized tamarack pulp, with or without 1% peroxide bleaching, with a pH varying from 3.5 to 10.5, and at both 23°C and 55°C (Table 1, all columns, two first sets of data versus two lasts), the higher the number of COOH groups, the higher the brightness. The ISO brightness which was measured was considerably low, as expected. The ISO brightness of unbleached pulp reaches 32 near pH 7 (table 1, column 3, data row 1), while the original COOH content approaches

152 mmol•kg^{-1} (table 1, column 3, data row 9). From our experiments, it was found that, as a rule, ozonization, followed or not by 1% peroxide bleaching, tends to increase the ISO brightness as well as the COOH content of the pulp. The relation is not linear, but a general trend is evident.

Carboxylic acids are the first really stable products of an oxidation reaction. They can be produced by oxidation of primary alcohols, aldehydes, ketones, alkylbenzene (with $KMnO_4$) and olefins with at least one hydrogen on the double bond (with $K_2Cr_2O_7$). For their part secondary alcohols are readily oxidized to ketones. Lignin is known to contain large amounts of primary alcohols, aldehydes and especially ketones. Ketones are also known to be more easily oxidized than alcohols.

Since ozone reacts very rapidly on the wood surface at high pulp consistency level [21], it can be concluded that the increase in COOH groups comes from the oxidation of the more sensitive ketone groups. Furman and Lonsky [7] and Lebo *et al.* [8] have demonstrated that a decrease in ISO brightness is accompanied by an increase in the number of quinoid structures in pulp. Quinones are known to be very sensitive ketone groups. Based on these facts, we propose that "the increase in ISO brightness should be accompanied by a decrease in the number of quinoid structures". This decrease in CO groups is measured as an increase of the COOH content, carboxylic acids being the result of the oxidation of quinones.

To measure the efficiency of ozone as a bleaching agent, we measured the ISO brightness as a function of ozone concentration. We used 2%, 4% and 6% of the ozone charge and compared the ISO brightness obtained as a function of both the pH of the pulp (table 1, columns 2-3-5-6, first set of data) and the temperature (table 1, columns 4-7, first set of data) of the ozonization reaction, followed or not by bleaching with 1% hydrogen peroxide (table 1, second set of data). As shown in Figure 5, the more the ozone, the brighter the pulp, as may be expected from a bleaching agent.

We also compared the various experiments of ozonization only with the control pulp at 0% ozone charge. Table 1 and Figure 5 show that the higher the pH is used, the more the ISO brightness increases. Even if the ISO brightness in an

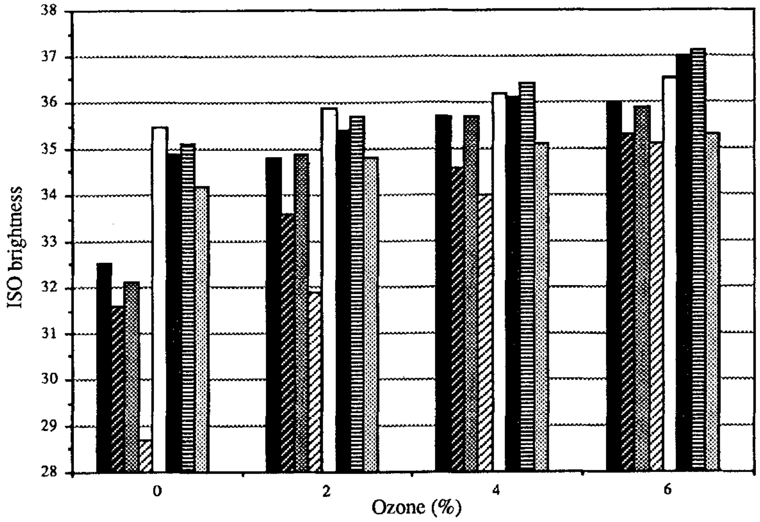

Figure 5. ISO brightness as a function of the ozone charge and pH. The ozone charge varied from 0% to 6%. Experiments at 23°C, ozonization only: ■ pH=3.5; ▨ pH=6.0; ▩ pH=8.0; ▧ pH=10.5. Experiments at 23°C, ozonization followed by 1% hydrogen peroxide bleaching: □ pH=3.5; ■ pH=6.0; ▤ pH=8.0; ▩ pH=10.5.

acidic media (before and after ozonization) reveals itself to be superior by 1 to 4 points to the one in an alkaline media, ozonization in the latter produces the best ISO brightness increase. Because alkali darkened the pulp, as shown in Figure 5, this result may indicate that the darker the pulp, the easier it is to bleach it. But it can also be an indication that the ozonization process is alkali dependent.

If ozonization is followed by a 1% hydrogen peroxide bleaching, the final ISO brightness result is higher. This is not a surprise in itself, but what is surprising is the fact that at a high ozone charge (6%), there is almost no difference between ozonized pulp and the one which was bleached after ozonization. This

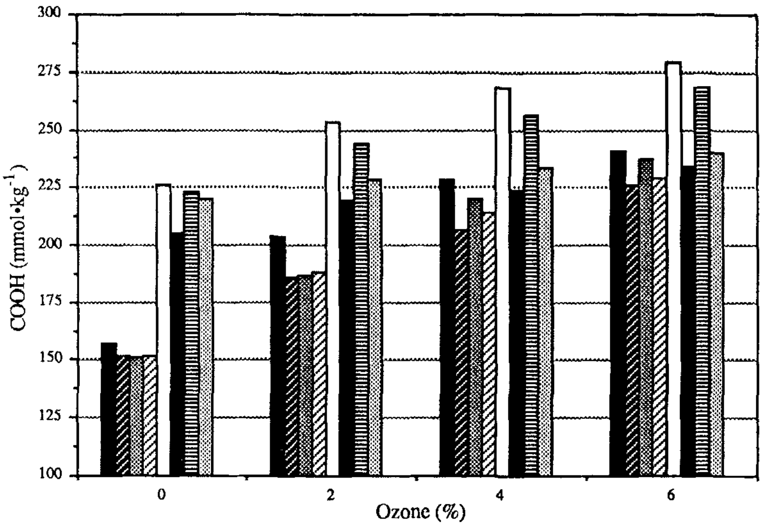

Figure 6. ISO brightness as a function of the ozone charge, pH and temperature. The ozone charge varied from 0% to 6%. Experiments with ozonization only: ■ pH=6.0 & T=23°C, ▩ pH=6.0 & T=55°C, ▦ pH=10.5 & T=23°C, ▨ pH=6.0 & T=55°C. Experiments with ozonization followed by 1% hydrogen peroxide bleaching: □ pH=6.0 & T=23°C, ■ pH=6.0 & T=55°C, ▤ pH=10.5 & T=23°C, ▦ pH=6.0 & T=55°C.

behavior is reflected in Figure 5, suggesting the inefficiency of a high charge of ozone as a pre-treating agent for hydrogen peroxide bleaching.

But can this inefficiency of a high charge of ozone as a pre-treating agent be overcome at a higher temperature? We tried to increase the temperature from 23°C to 55°C (table 1, columns 3-6 versus columns 4-7, two first sets of data) . The results appear in Figure 6. It is obvious from our results that an increase in temperature has no noticeable effect on the ISO brightness of the pulp. An increase of less than 1 point being meaningless in this case. Figure 6 also shows that the behavior of the pulp, with respect to pH, ozone charge and hydrogen peroxide bleaching, remains the same either at 23°C or 55°C.

From this first set of experiments, one can see that the ozone treatment should be carried out at an acidic pH to obtain the best ISO brightness. In addition, an alkaline treatment of the pulp with ozone improves ISO brightness the most, in absolute values. At a pH of 3.5, a 4% ozone charge produces an increase of 3.2 ISO points. If the same treatment is applied on an alkaline pulp at a pH of 10.5, the increase is 5.3 points, but the resulting ISO brightness is inferior to that of an acidic pulp by 1.7 point. These results are almost identical to the ones obtained from a pulp that has not been ozonized, but that has been bleached with 1% hydrogen peroxide. Therefore, as for ISO brightness, the use of ozone as a treatment on a tamarack TMP pulp is ineffective, because 1% hydrogen peroxide bleaching provides the same results as a 4% ozone treatment.

Let us now examine the relationship between the COOH content of the pulp and the variations in the ozone charge, pH (table 1, columns 2-3-5-6, third set of data), temperature (table 1, columns 4-7, third set of data) and hydrogen peroxide bleaching (table 1, fourth set of data). We will begin with the amount of COOH groups as a function of the ozone charge and pH. These results are shown in Figure 7.

The amount of COOH groups for an unbleached pulp does not vary as a function of the pH. The COOH content increases 1.5 fold when the applied ozone charge reaches 6%, and the rate of this increase is almost linear. The use of 1% hydrogen peroxide bleaching after ozonization results in a more chaotic behavior. The amount of COOH groups increases slightly, but with no evident correlation with the pH. This behavior, dissimilar to the one shown by ISO brightness, suggests that CO groups are not entirely responsible for the yellowing of the pulp. We postulated earlier that the increase of COOH groups is due to the decrease of CO groups or quinones. Since the amount of COOH groups and, therefore, quinones, is pH independent, one must conclude that there are other chromophoric groups in the TMP of tamarack. These other chromophoric groups exhibit a pH dependence behavior, which is why ISO brightness is a function of pH. This may

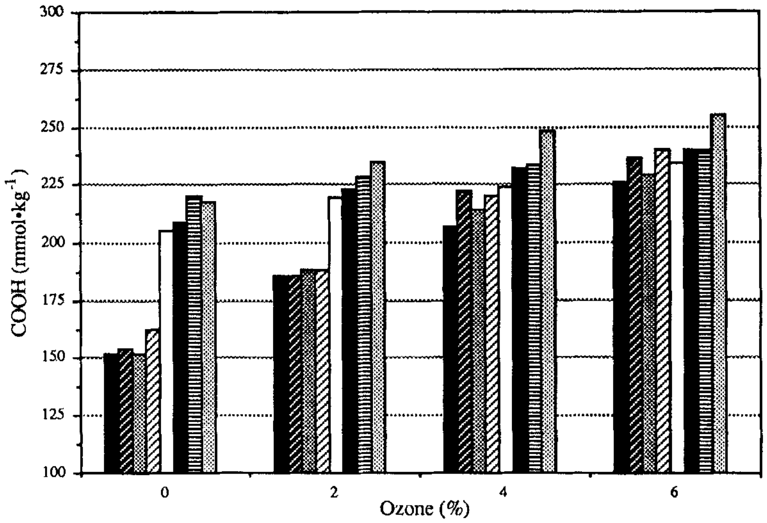

Figure 7.Carboxylic acid content as a function of the ozone charge and pH. The ozone charge varied from 0% to 6%. Experiments at 23°C, ozonization only: ■ pH=3.5; ▩ pH=6.0; ▦ pH=8.0; ▨ pH=10.5. Experiments at 23°C, ozonization followed by 1% hydrogen peroxide bleaching: □ pH=3.5; ■ pH=6.0; ▤ pH=8.0; ▩ pH=10.5.

be the explanation of the unperfected linear relationship between the ISO brightness and the COOH content presented in Figure 4.

We know that ozone attacks the quinolic structures, thus producing COOH groups. This reaction is pH independent. But we can also see the non-specificity of this attack, as ozone also reacts with other chemical groups, which are not quinones, but are colored. This reaction, unlike the one involving quinones, is pH dependent. We said that ozonization may be alkali dependent, and it seems that the ozone attack on these other chromophores is this pH dependent reaction. On the other hand, it is possible that these reactions are slower than the one observed with

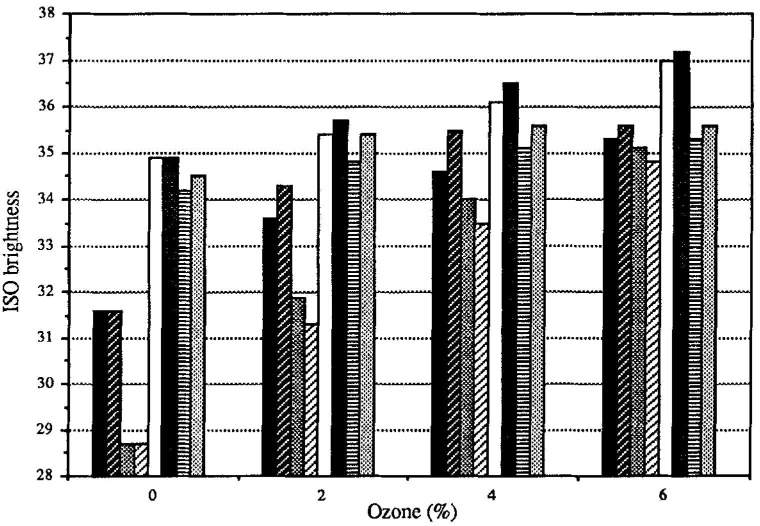

Figure 8. Carboxylic acid content as a function of the ozone charge, pH and temperature. The ozone charge varied from 0% to 6%. Experiments with ozonization only: ■ pH=6.0 & T=23°C, ▨ pH=6.0 & T=55°C, ▩ pH=10.5 & T=23°C, ▧ pH=6.0 & T=55°C. Experiments with ozonization followed by 1% hydrogen peroxide bleaching: □ pH=6.0 & T=23°C, ■ pH=6.0 & T=55°C, ▤ pH=10.5 & T=23°C, ▦ pH=6.0 & T=55°C.

quinoid groups. This way, the reaction time may be long enough for us to observe partial auto-oxidation of ozone as the pH is increased [21]. Based on previous results obtained elsewhere [21] we do not think this is the case, but unfortunately, our experiments do not allow us to remove this ambiguity.

We also modulated the temperature of the pulp (table 1, columns 3-6 versus columns 4-7, last two sets of data), as we did previously with ISO brightness measurements. These results are shown in Figure 8. From these results, it is clear that temperature between 23°C and 55°C have no effect on the COOH content of the pulp, with or without ozone, and with or without hydrogen peroxide, at either pH=6.0 or pH=10.5. This is similar to the results we obtained with ISO brightness.

CONCLUSION

Based on our study of the influence of ozone on the optical properties of a tamarack's TMP pulp, some clear results can be drawn. The use of ozone increases the ISO brightness of the pulp. This bleaching effect is found to be pH dependent, and most effective in acidic media. Alkaline pH, on the other hand, produces the best ISO brightness increase in absolute values from a control experiment, but the resulting brightness is still inferior to the one obtained at acidic pH. Temperature, ranging from 23°C to 55°C, has no effect on the brightening effect of ozone. We also discovered that we needed almost 6% of ozone to obtain the same bleaching effect as 1% of hydrogen peroxide.

It is true that ozone attacks CO groups, mainly quinones (Lebo *et al.*[8]) producing COOH groups, as a result. But our experiments show that the production of COOH groups is not pH dependent. This discrepancy between the behavior of ISO brightness and the COOH content, despite the observed relation between the two, indicates that ozone indeed lacks the chemical selectivity required of a good bleaching agent.

In conclusion, ozone is not efficient as a bleaching agent for a TMP pulp of tamarack. However, ozone can have other interesting applications, e.g. the mechanical properties of the pulp. These properties will be investigated in a future study.

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