

CHANGES ON FIBER SURFACE DURING PREBLEACHING COMPARING, DIFFERENT CHLORINE-FREE DELIGNIFICATION AGENTS

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ABSTRACT

Three methods for surface characteristics of fibers were used (selective staining of fibers, ESCA measurements, and charge determination) to follow the delignification process during prebleaching with ozone and peroxide. The results of each method were evaluated with respect to the particular action of each agent. The method of selective staining with cationic dyes offers us a simple way to characterize the reactivity of fiber surface covered with lignin. The cationic dyes' absorbancies are in correlation with the amount of active sites that belong to lignin (mostly phenolic groups), representing the differences between the course of delignification caused by either ozone or peroxide.

Keywords: Selective staining, ESCA measurements, charge determinations, prebleaching, ozone, peroxide.

INTRODUCTION

Because of increasingly restrictive laws regulating waste water quality from pulp and paper mills, chlorine-free chemicals are very often used as delignification and bleaching agents to a great extent. The most common among them are oxygen, peroxide, some peroxy acids, and ozone. Each of them has its specific way of action on the fiber surface during the process.

Bleaching of pulp is a continuous sequence of nucleophilic and electrophilic reactions of bleaching chemicals (Annergren et al. 1998), mostly with lignin and to a lesser extent with carbohydrates, provided that selectivity is optimal (Gierer 1990).

Chlorine-free bleaching of kraft pulp begins with extended oxygen delignification, which is, in fact, a continuation of the nucleophilic kraft

pulping process. It is a radical acidic reaction, where two reagents with different reactivity levels take part: a) hydroxyl radical with high oxidative power reacting with phenolic and non-phenolic lignin structures, and b) less aggressive oxygen reacting only with phenolic lignin structures. During the reactions, new chromophore groups of quinone type are formed. Some of them are released with conjugated addition and further on with oxidation (Eckert et al. 1973; Gierer and Imsgard 1977).

In the case of the Cl-free bleaching process, two different agents can be used after the extended delignification stage: ozone or peroxide.

Ozone is a cationic electrophilic bleaching reagent. It reacts with aromatic and olefinic structures. Ozonolysis results in a cleavage of original aromatic or olefinic double bonds, and formation of carbonyl containing fragmentation

products (aldehydes, ketones, and/or acids, etc.) (Huisgen 1963).

Hydrogen peroxide is a competitive bleaching agent to ozone. It promotes anionic nucleophilic bleaching processes for which carbonyl and conjugated carbonyl structures, present in native lignin, are the targets. These structures can also be formed during delignification and bleaching processes, or during radical intermediate processes (Adier 1977). Carbonyl groups can be found in the side chain of the phenyl propane unit, or they are the quinone or quinone methide types derived from aromatic structures. During peroxide reaction, the side chain of phenyl propane lignin structure cleaves, whereas the ring's quinone structure is preserved. In addition, the aromatic ring tends to open during the alkaline heterolytic cleaving of C-C bonds (Gellerstedt and Agnemo 1980).

Bleaching selectivity

The bleaching process is expected to remove mainly the lignin compounds and/or the chromophore groups and not to affect the structure of carbohydrates. Because of high electronic density, the aromatic rings and aliphatic double bonds present in residual lignin are the targets for electrophilic oxidative and acidic bleaching agents (deBelder et al. 1963). However, oxidative radicals originating from bleaching agents can attack cellulose and hemicellulose chains as well. They can abstract hydrogen atoms not only from the lignin side chain but also from hydroxy alkyl group in carbohydrates. This reaction leads to a formation of carbonyl groups in carbohydrates (in case of lignin the formation of α -CO groups). If this reaction is followed by alkali extraction or alkali delignification, the β -elimination takes place in the pyranose ring (i.e. peeling) (deBelder et al. 1963).

OBJECTIVES

The aim of this work is to compare the occurrences on fiber surface during prebleaching carried out with ozone or peroxide. Three different

methods were used for fiber surface characterization: selective staining of fiber, ESCA measurements, and determinations of total charge of fibers. Some standard methods for fiber analyses were also applied.

MATERIALS AND METHODS

Fibers

Kraft pulp samples, additionally delignified by oxygen, were prebleached with peroxide and ozone as described previously (Drnovšek and Perdih 2000). Nine fiber samples were prepared. They were labelled according to the prebleaching agents used: oxygen sample (O) with kappa No 12.1; peroxide samples (P) with kappa No 10.4, 8.5, and 7.1, respectively; and ozone samples (Z) with kappa No 10.8, 8.8, 6.7, and 3.2, respectively. All samples were acidified before being tested with diluted sulphuric acid to pH 4.5.

Selective staining the fibers

The principle of this method was developed with the reference fibers: 1) unbleached softwood kraft pulp with lignin; 2) the same pulp treated with permanganate to remove lignin (hemicelluloses and cellulose part of fibers), and 3) alpha cellulose component prepared by the Tappi standard method from the pulp already treated with oxygen and ozone with kappa No 3 (presenting cellulose component in the fibers). Three groups of dyes were used: 1) dyes with good affinity for the lignin part of fibers (cationic dyes); 2) dyes with good affinity for hemicelluloses (cationic phthalocyanine dyes); and 3) dyes with the affinity for alpha cellulose in fibers (direct dyes).

The complete method was carried out with never-dried fibers. The preparation of dyes' solutions, staining procedures, and the procedure of measuring the color intensity of stained fibers have been described elsewhere (Drnovšek and Perdih 2000).

The cationic dyes selective for lignin used in our experiments are outlined in Table 1.

TABLE 1. *Cationic dyes used for selective staining.*

Dye, Color Index No	Selectivity L/H*
Crystal Violet, C.I. 42555	2819
Methylene Blue, C.I. 52015	1530
Safranin O, C.I. 50240	499
Acridine Orange, C.I. 46005	2.3

*Selectivity L/H is defined as the ratio of absorbancies (in Kubelka-Munk units) of dyed lignin containing fibers (kraft pulp, kappa No = 18) and dyed lignin-free fibers (the same kraft pulp treated with KMnO₄) (Drnovšek and Perdih 2001).

Relative half-span, rhs (%) of the results of unstained fibers (R_0) were for the samples: oxygen, O (kappa No 12.1) 1.1%; for ozone samples (kappa No 10.8, 8.8, 6.7, and 3.2) 5.9, 10.2, 5.9 and 11.5%; and for peroxide samples (kappa No 10.4, 8.5, and 7.1) 6.6, 4.4, and 4.7%, respectively. Except for the oxygen sample, these values were not exceeded in the results of stained fibers with selected dyes.

ESCA measurements (XPS X-ray photoelectron spectroscopy)

Handsheets of fibers were made according to SCAN-C 26; 76, and extractives were removed from the sheets with DCM in the Soxhlet apparatus according to standard SCAN-C 7: 62. ESCA measurements were performed with the Kratos Analytical AXIS 165 electron spectrometer using a monochromated Al K α X-ray source. Survey scans were taken with a 1.0 eV step and 80 eV analyzer pass energy. The high resolution regional spectra were recorded with a 0.1 eV step and 20 eV pass energy. The emission angle was 90° with respect to the sample surface. This corresponds to a maximum sampling depth of ca 10 nm. The survey scans and the high resolution regional spectra of three measurement points were recorded in order to obtain the average of the sample's heterogeneity. The relative amounts of differently bound carbons were calculated by the Gaussian curve in correspondence with the high-resolution Cls peak. The chemical shifts relating to C-C (C1), C-O (C2), O-C-O or C=O (C3), and O=C-O (C4) were 1.7 eV, 3.1 eV, and 4.4 eV, respectively. The whole procedure has

been described elsewhere (Johansson et al. 1999. The relative half-span (rhs)) of the measuring results for Cl values was 6.7%, for C2 values 0.65%, for C3 values 1.2%, and for C4 values 8.7%.

Polyelectrolyte titration

This method is based on the transformation of carboxylic groups on the fiber surface into their Na⁺ form, followed by the treatment of fiber suspension by a cationic polymer with defined average molecular weight, and by retitration of the remains of the cationic polymer with anionic K-polyvinyl sulphate (Wagberg et al. 1989).

The preparation of the fiber suspension and all further procedures for determination are described elsewhere (Laine et al. 1996). In the research described in this paper, the solution of a low molecular mass polyelectrolyte Polybrene (poly 1,5-dimethyl-1,5-diazaundecamethylene bromide), $M^w \approx 8000$ was used to determine the total charge of fibers.

The relative half-span (rhs), % of the results of the polyelectrolyte titration; for oxygen sample, O (kappa No 12.1) rhs was 0.1% for ozone samples, Z (kappa No 10.8, 8.8, 6.7, and 3.2) rhs were 9.5, 11.9, 11.9, and 2.5%; and for peroxide samples, P (kappa No 10.4, 8.5, and 7.1), they were 5.4, 10.1, and 5.3%, respectively.

Standard methods

The standard methods conducted in fiber suspensions were: Kappa number, ISO 302-198; viscosity, ISO 5351/1-1981; carbonyl groups (Browning 1967); hexenuronic acids (Gellerstedt and Li 1996).

RESULTS

The samples were prebleached in order not to lose too much yield or too many mechanical properties of the fibers. The results of standard analyses, applied to characterize the basic properties of selected pulp sheets, are outlined in

TABLE 2. Basic characteristics of pulp samples.

Samples	Kappa No	HexA, mmol/g	Kappa No _{corr.}	Viscosity, ml/g	Selectivity factor*	Carbonyl groups, mmol/100g
O (oxygen)	12.1	3.37	11.8	699	1.7	2.00
P (peroxide)						
P1	10.4	3.87	10.1	723	1.4	2.05
P2	8.5	3.99	8.2	688	1.2	1.81
P3	7.1	3.82	6.8	683	1	1.42
Z (ozone)						
Z1	10.8	3.65	10.5	715	1.5	2.18
Z2	8.8	2.96	8.6	670	1.3	2.27
Z3	6.7	2.63	6.5	453	1.4	2.88
Z5	3.2	1.44	3.1	354	0.9	4.79

* $k_{\text{corr}}/\text{visc.} \cdot 100$

TABLE 3. Results of ESCA measurements and charge determinations.

Samples	Kappa No _{corr.}	Total charge, μmol/g	$\Phi_{\text{lig.}}$ %	O/C	C1, %	C2, %	C3, %	C4, %
O (oxygen)	11.8	78.22	14.7	0.713	9.21	71.32	18.2	1.28
P (peroxide)								
P1	10.1	79.87	15.5	0.702	9.57	71.35	17.748	1.32
P2	8.2	77.79	12.4	0.705	8.09	72.47	18.11	1.33
P3	6.8	80.05	12	0.720	7.88	72.82	18.07	1.24
Z (ozone)								
Z1	10.5	76.46	13.7	0.707	8.69	72.25	17.81	1.25
Z2	8.6	80.05	8.9	0.746	6.36	74.05	18.33	1.26
Z3	6.5	84.05	9.8	0.738	6.79	73.72	18.27	1.22
Z5	3.1	67.03	11.6	0.728	7.7	73.01	18.1	1.19

Table 2. The results of total charge of fibers and ESCA measurements are presented in Table 3. All the results of staining with the selected group of dyes are given in Table 4.

Comparison of ESCA measurements with kappa No.

The values of ESCA C1, representing changes in lignin content in correlation with kappa No, which have already been corrected for the hexenuronic acid content (Li and Gellerstedt 1998), decrease between kappa No. 11.8 and 8.6 during ozone prebleaching, as shown in Fig. 1. Below kappa No 8.6, they start to increase. The situation is slightly different with peroxide prebleaching where C1 values first show a slight increase and then a decrease with delignification. In both cases, a change at the approximate level of

kappa No 8 can be noticed. The relationship between ESCA C4 values, representing the content of carboxylic groups, and kappa No (Fig. 2) shows an almost linear decrease in the case of ozone prebleaching, while with the use of peroxide, first an increase and below kappa No 8.2 a decrease is observed.

The relationship between ESCA C3 values, representing the O–C–O and C=O groups, and kappa No (Fig. 3) is similar comparing both prebleaching agents. The curves decrease from kappa No 11.8 to around 10, then they increase to kappa No around 8, after which they both decrease again in both cases. The C3 values do not correlate with the amount of carbonyl groups, determined chemically with hydrazine (Fig. 4). It shows an interesting pattern of the curves presenting the dependencies of carbonyl groups and C3 values. The same shape of the curves present-

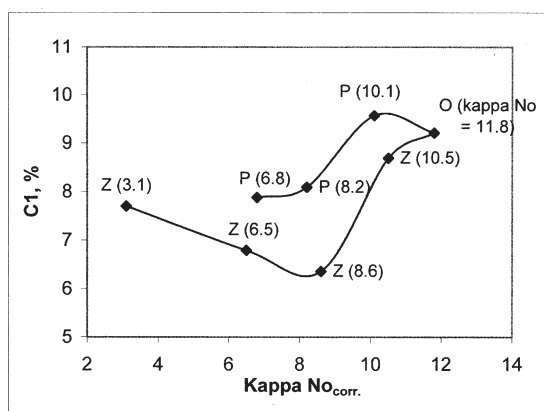


FIG. 1. Value of ESCA C1 during prebleaching.

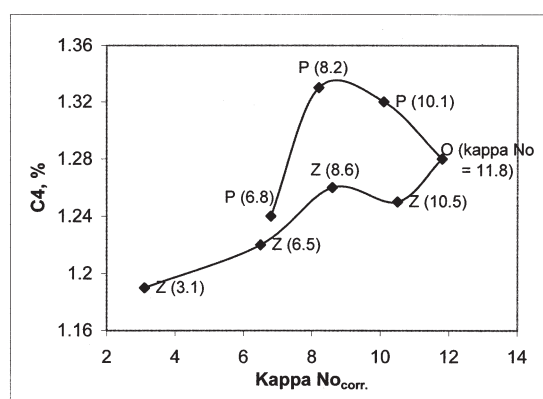


FIG. 2. Value of ESCA C4 during prebleaching.

TABLE 4. Staining results (absorbance in Ku-Mu units at $\lambda_{\max}$)

Samples	Kappa No _{corr}	Methylene Blue	Safranin O	Crystal Violet	Acridine Orange
O (oxygen)	11.8	1.048	0.947	3.246	3.114
P (peroxide)					
P1	10.1	0.687	0.583	2.126	2.572
P2	8.2	0.276	0.413	2.020	2.315
P3	6.8	0.150	0.253	1.342	1.988
Z (ozone)					
Z1	10.5	1.015	0.769	2.928	2.834
Z2	8.6	0.308	0.209	0.882	1.726
Z3	6.5	0.132	0.143	0.626	1.365
Z5	3.1	0.020	0.023	0.077	1.096

ing C3 values can be noticed in relation to both prebleaching agents, but there is a different trend for the values of the carbonyl groups. The content of carbonyl groups increases during ozone prebleaching, while it decreases during peroxide prebleaching.

The ESCA ratio O/C is also changing during prebleaching. During ozone and peroxide prebleaching, it drops from kappa No 11.8 to 10.5. Afterwards, in the case of ozone action, it rapidly increases to kappa No 8.6, and then again decreases slowly toward kappa No 3. In the case of the peroxide prebleaching, the ratio grows continuously from kappa No 10 to 7.

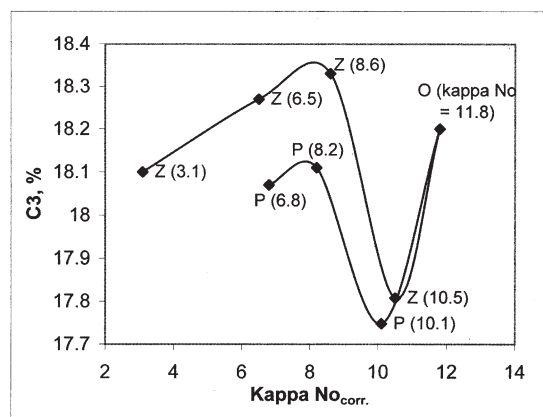


FIG. 3. Value of ESCA C3 during prebleaching.

Relationship between total charge of fibers and cationic dyes' absorbancies

Figure 5 presents the dependence of cationic dyes' absorbancy to the total charge of fibers during ozone prebleaching. From kappa No 11.8 to 6.5 the absorbancy drops fast, while the total charge of fibers slightly decreases at first and then increases toward kappa No 6.5. The absorbancies of cationic dyes do not change anymore below kappa No 6.5. However, the total charge of fibers evidently decreases, indicating that there are obviously certain processes developing on carbohydrates in this part of delignification. On the contrary, the figure presenting peroxide prebleaching does not show any rela-

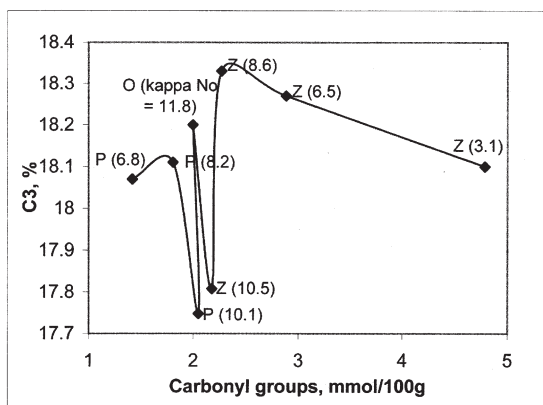


FIG. 4. Carbonyl groups during prebleaching in comparison with ESCA C3 values.

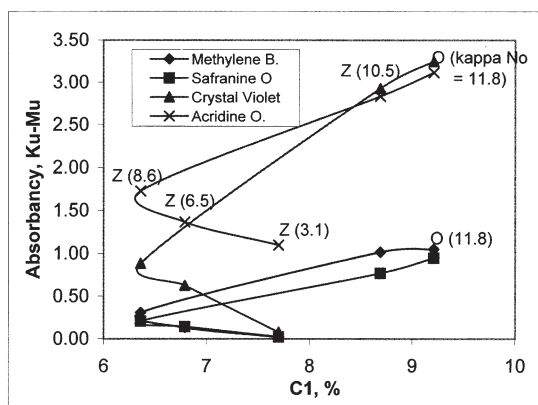


FIG. 6. Comparison between ESCA C1 values and absorbances of cationic dyes during prebleaching with ozone.

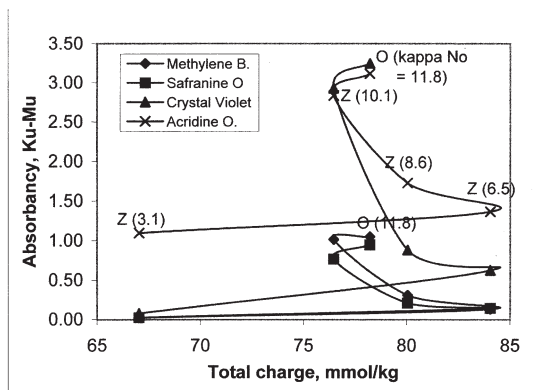


FIG. 5. Comparison of total charge with cationic dyes' absorbance during prebleaching with ozone.

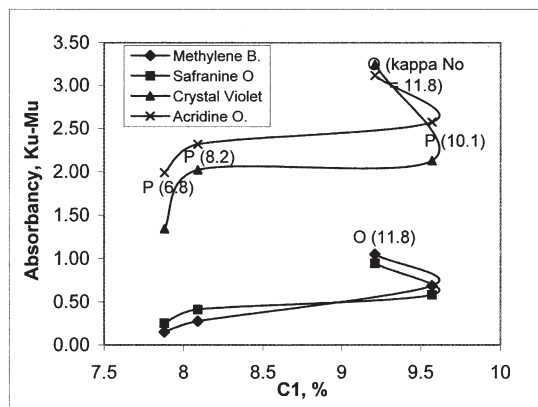


FIG. 7. Comparison between ESCA C1 values and absorbances of cationic dyes during prebleaching with peroxide.

tionship between these two parameters (figure not shown).

Comparison of ESCA C1 values and cationic dyes' absorbances

In Fig. 6, which shows the dependence of C1 values and cationic dyes' absorbances during the ozone prebleaching, changes occur at the point of kappa No 8.6. Before this, C1 and the absorbances decrease. Below kappa No 8.6, C1 values increase, while the absorbances decrease with further delignification. Figure 7 presents the same dependence during peroxide prebleaching, but the curves show the opposite situation.

C1 values increase from kappa No 11.8 to 10; then they decrease from kappa No 10 to 8 with no changes in absorbances. Below kappa No 8, C1 values as well as absorbances decrease.

DISCUSSION

The main interest of this study was to evaluate the differences between the actions of two different prebleaching agents using three different methods for fiber surface characterization. The purpose was also to define the main advantages for each method. Looking at the ozone process, ESCA C1 values (C not bound to O) should corre-

spond to the amount of lignin. However, at kappa No 8.6 it starts to increase (Fig. 1), meaning that below kappa No 8.6, changes on carbohydrates take place to a greater extent than on lignin. A similar situation is indicated by the ESCA O/C ratio. This indicates that the delignification process continuing on until kappa No 8.6 is reached (by ozone treatment), after which degradation of the carbohydrates takes place. This conclusion is corroborated in Fig. 8, where the decrease of viscosity indicates degradation of the carbohydrate polymers. Therefore, a better method for observing lignin removal is the staining of fibers with cationic dyes where the absorbance's decrease during the whole process can be determined. This can be explained by a decreasing amount of phenolic groups—measure for lignin reactivity. The cationic dyes are bound to the phenolic groups and show good selectivity for lignin (Drnovšek and Perdih 2001). The difference in cationic dye absorbancies between ozone and peroxide treatments shows that more active groups remain on the fiber surface during peroxide treatment (higher absorbancies at the same kappa No) than during ozone treatment.

The amount of ESCA C4 values (carboxyl groups) decreases constantly during ozone prebleaching (Fig. 2) because ozone attacks these groups regardless of whether they belong to lignin or carbohydrates. The situation is different

with the peroxide process where the C4 increases at first (i.e., peroxide initially causes the formation of new carboxylic groups). However, the amount of C4 value starts to decrease afterwards, coming close to the amounts that are measured for ozone delignification (Fig. 2). These values cannot be additionally clarified by the staining results, although they do indicate that the dyes do not interact well with carboxylic groups. Similarly, ESCA C3 values change, following either ozone or peroxide treatments (Fig. 3). However, there is no correlation with the amount of carbonyl groups determined chemically (Fig. 4). These groups are constantly formed during ozone action on fibers and are removed during peroxide treatment (Gierer 1990), which cannot be explained either by ESCA or by the present staining results.

Figure 5 shows that there is also no correlation between the staining results and the total charge offibers, the latter being represented by ionizable groups on the accessible fiber surface. Determining the charge of fibers reflects the dissociation of anionic groups on fiber surface. Dissociation is forced by a reagent or a high pH during the procedure. On the other hand, by staining of fibers at pH 5, the tested cationic dyes detect active groups in phenolic form, which are mostly undissociated.

Figure 6 shows that in the case of ozone action, a real delignification process takes place on the fiber surface until kappa No 8.2 is reached. After this, changes occur predominantly on carbohydrates. The same indication is shown by Fig. 1 as well as by the decreasing values in viscosity (Table 1, Fig. 8). However, the course of delignification proceeds differently during peroxide action (Fig. 7). Both an increase in ESCA Cl from kappa No 11.8 to 10 (also a slight increase in viscosity), and a strong decrease from kappa No 10 to 8 with practically no loss in the active sites on fiber surface (no change in cationic dyes' absorbancies) can be seen as well. Thus, delignification with peroxide occurs on non-phenolic sites of lignin molecules (Eckert et al. 1973). Below kappa No 8, a decrease of absorbancies with Cl values is noticed. Further delignification with peroxide is not recom-

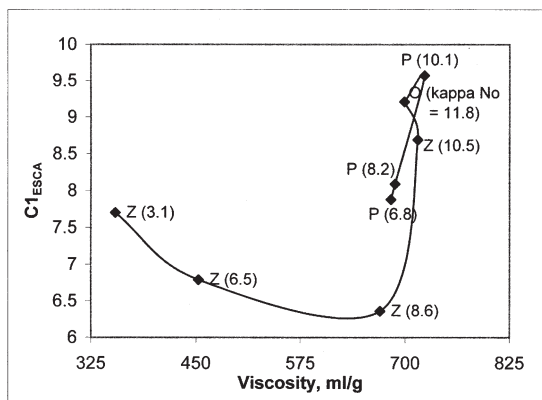


FIG. 8. A decrease of pulp viscosity in comparison with ESCA C1 during prebleaching.

mended because of the unacceptably long reaction time, high temperature, and other costs.

CONCLUSIONS

The absorbance of cationic dyes provided a good insight into what is happening with lignin on the fiber surface during prebleaching. In addition, it offers the best information for the three different methods (also ESCA and charge determination) concerning the difference between the actions of two delignification agents. The values of absorbancies indicate the presence of phenolic groups on the fiber surface, which belong to lignin. Because the presence of these groups is higher using peroxide treatment (higher absorbancy values in comparison with ozone treatment at the same delignification degree), it can be confirmed that delignification with peroxide occurs by the action on non-phenolic sites which react with hydroxyl radicals formed during nucleophilic reactions. Therefore, more phenolic groups are present on the fiber surface at the same kappa level for peroxide treatment than during ozone treatment. The presence of these groups is important for further delignification or bleaching processes; i.e., they are able to form the bonds between fibers themselves or fibers and paper additives during paper sheet formation.

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