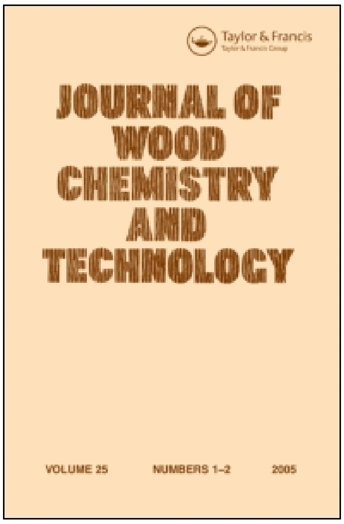

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M. M. Sain[a]; C. Daneault[a]; M. Parentaeu[a]
[a] Pulp and Paper Research Center, Universite du Quebec a Trois-Rivieres, Quebec, Canada

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ELIMINATION OF CHROMOPHORES FROM SECONDARY FIBER OF WOOD MECHANICAL PULP. I. EFFECT OF ZEOLITE ON HYDROGEN PEROXIDE BRIGHTENING

M. M. Sain, C. Daneault, and M. Parentaeu

Pulp and Paper Research Center, Universite du Quebec a Trois-Rivieres, Quebec

Canada G9A 5H7

ABSTRACT

The effect of zeolites on hydrogen peroxide brightening of secondary fiber from wood mechanical pulp was investigated by studying which chromophores were eliminated in the process. The effects of the type of zeolite, reaction time, and concentration of peroxide were examined. A combination of Na-A zeolite or phosphoric acid-treated zeolite with hydrogen peroxide promoted elimination of chromophores. The time dependence of the chromophore elimination reaction was investigated by following the change in the intensity of characteristic IR bands in a frequency range attributed to quinonoid structures and α,β-unsaturated carbonyl groups. The addition of zeolite to the peroxide enhanced brightening of the pulp by improving the light reflectance at 457 nm, a change potentially attributable to a decrease in chromophoric quinonoid structures.

INTRODUCTION

Elimination of chromophores from waste wood mechanical pulp requires a substantial extension of the present knowledge of chromophores that are responsible for the typical yellow-brown color of the pulp. It is crucial to determine the nature of the chromophores that contribute to the color of the wood

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and understand the mechanism of the discoloration reaction. In recycling wood pulp-based paper which is essentially a mixture of thermomechanical pulp (TMP), ink, adhesives, and fines, the coloration is influenced not only by the chromophores in the pulp but also by other coloring matter present in the waste furnish. The spectroscopic methods used to evaluate brightening of pulp are based on the absorption of light at 457 nm. At this wavelength most of the color also strongly absorbs light and therefore, chromophores can not be evaluated by UV spectroscopic methods in peroxide treatments of recycled wood pulp

One area that has received little attention is the study of how secondary fibers of mechanical pulps respond to peroxide treatment in the presence of chemicals other than the sodium silicate used to stabilize the peroxide. It is well known that sodium silicate is an effective stabilizer for peroxide in chromophore elimination reactions. Sodium silicate acts as a metal deactivator by forming complexes with metals such as Mn, Cu, and Fe. It also buffers the pH during reaction of chromophores with alkaline peroxide.[1-5] Zeolites have some properties similar to sodium silicate.[6] The typical properties of a Na-A zeolite are listed in Table 1.

The sodium aluminosilicate zeolites, which consist of 17% Na_2O, 33% SiO_2, and 28% Al_2O_3, are essentially micro particles. Dispersed in water they yield an alkaline suspension with a pH ranging from 10 to 11. They possess good ion exchange capacity. Unlike an alkaline suspension of sodium silicate, their water insolubility limits their diffusion into the wood fiber. Zeolites possess some other unique properties relative to sodium silicate. Due to their porous nature, they are light and easy to separate by methods employing specific gravity differences. They can adsorb considerable polymeric material from an aqueous wood pulp suspension.[7] Finally, their ion exchange or catalytic properties can be custom designed for specific reactions by either reduction or oxidation.[8] Properly designed zeolites could then improve the efficiency of peroxide stabilization as well

Table 1

Typical Properties of Na-A Type Zeolite

Form	Free flowing powder
Color	White
Crystal structure	Cubic
Bulk density	0.40-0.48 g/cm^3
Mean particle size	3-6 microns
pH of 1% dispersion	10-11
Nominal pore size diameter	4.2 Å
Ion exchange capacity	5.6 mEq/g hydrated zeolite

as activate hydrogen peroxide reactivity[9] toward chromophore modification and/or elimination from wood pulp.

The purpose of this study was to determine the role of Na-A zeolite, either modified or unmodified, on the elimination of chromophores from a recycled wood pulp-based paper furnish with hydrogen peroxide.

EXPERIMENTAL

Unless stated otherwise, the sodium silicate used throughout the study was a clear alkaline solution with about 11% NaOH content. The ratio of SiO_2 to Na_2O was approximately 3:1. The zeolite used was detergent grade (Vulcafor A) Na-A type zeolite. The hydrogen peroxide was a stabilized 50% solution. The paper furnish composition was 50% local offset-printed unbleached TMP newsprint and 50% toner printed bleached chemical pulp-based office waste. Deionized water was used throughout the experiments. All other chemicals used in the study were reagent grade, supplied by various manufacturers.

Zeolite Modification

Na-A zeolite was treated with phosphoric acid in two stages. In the first stage 10% (wt) phosphoric acid was added and the product was allowed to condition at room temperature for several hours. After a given time period, the zeolite containing phosphoric acid was heat-treated, initially at 105°C for a predetermined time and then at about 250°C in presence of sodium hydroxide. The first heat treatment with phosphoric acid removes one mole of water[10] Paper chromatographic analysis confirmed that the initial heat treatment of phosphoric acid resulted in elimination of water from a part of the orthophosphoric acid. The converted phosphoric acid was a mixture of about 43% pyrophosphoric acid, 17% ortho-, 23% tripoly-, 11% tetrapoly-, and a lesser amount of pentapolyphosphoric acid.[10] The chance of formation of the sodium salts can not be eliminated altogether as the heat treatment process was carried out by first adsorbing phosphoric acid on a Na-A type zeolite. Figure 1 shows the IR spectra of the heat treated samples as well as unmodified Na-A zeolite in KBr. A strong absorption band in the frequency range 1300-1150 cm^{-1} confirms the double bond of the pentavalent phosphorous compound (sample zeoP).[11] A broad band near 1100-1000 cm^{-1} which overlapped with the absorption band near 1300-1150 cm^{-1} points to the possibility of inorganic phosphates such as the Na-salts of phosphoric acid.[11] The absorption bands near 1286, 1174, and 980 cm^{-1} are essentially stretching vibrations for phosphorous pentoxide, orthophosphoric acid and phosphate compounds. The IR study suggests that the phosphoric acid probably reacted with sodium in Na-A zeolite even in the first stage of the heat treatment process. The second stage heat treatment at 250°C in the presence of sodium hydroxide did not cause much change in the composition as evident from the IR spectrum (zeoHP) in Figure 1. The minor changes were an increase in the band intensity near 1020 cm^{-1}, attributable to formation of more inorganic phosphoryl-containing ions, and a marginal decrease in the band intensity near 970-930 cm^{-1}, assigned to pyrophosphate.[12] Based on these observation we propose reaction scheme I with the additional formation of glassy sodium metaphosphate and tetrasodium polyphosphate.[13]

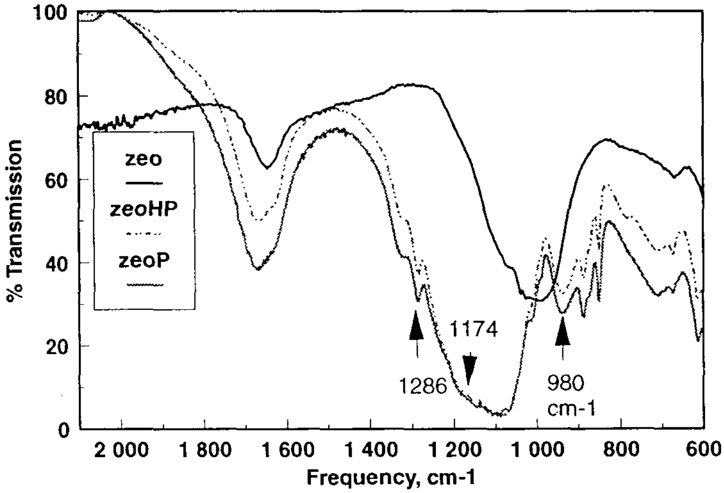
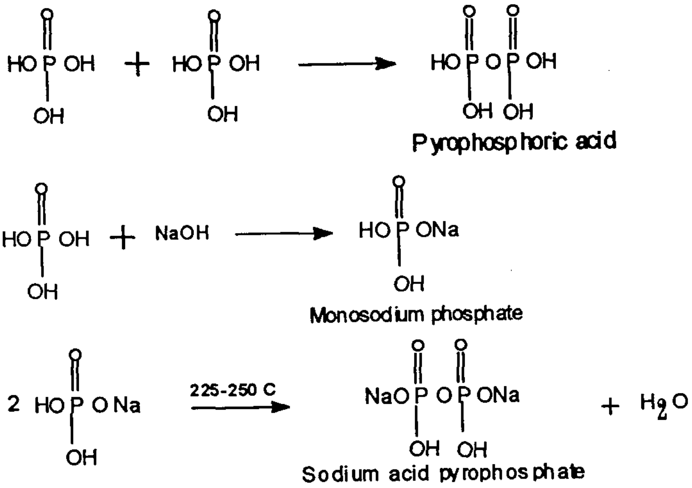


Figure 1. FTIR Spectra of Na-A zeolite (zeo), phosphoric acid treated Na-A zeolite before heat treatment (ZeoP), and after heat treatment (zeoHP).



Scheme I

Pulping

The waste paper was pulped in a pulper using a helical rotor. The rotor speed was about 1000 rpm. The repulping conditions are shown in Table 2. A mixture of newsprint and photocopy paper was added to the pulper at 8% consistency. The pH was adjusted with NaOH and pulping was carried out for 20 min. The consistency of the pulped slurry was increased to 12% by draining water. This slurry was then used for flotation or peroxide treatment.

Peroxide Treatment

The pulped secondary wood fiber was treated with peroxide in the presence or absence of other chemicals such as peroxide stabilizer, sodium hydroxide, zeolite, or chelating agent. The general peroxide treatment conditions are shown in Table 2. The chelating agent used was DTPA (0.5%). It was added with the peroxide and other chemicals. Zeolite or modified zeolite was added before any pH adjustment. The pH was measured on bleach liquor filtrate. The accuracy of the pH measurement was ±0.05. The conditions for peroxide treatment are shown in Table 2. Peroxide treatments were done in polyethylene bags. During the course of the bleaching reactions, samples of bleach liquor were collected for determining the residual peroxide content as a function of time. After the peroxide treatment, the pulp was washed thoroughly to remove residual chemicals and then conditioned and stored for further use. Each experiment was repeated twice to obtain average values. A small portion of the pulp was used to determine chromophore concentration by FT-IR and reflectance methods.

Flotation

Before and after the peroxide treatment the pulp was subjected to flotation in a 6.5 L Open Lead flotation cell. About 1% Na-oleate, as the collector, was dispersed in a 0.8% pulp slurry. About 180 ppm of Ca was then added as $CaCl_2$ and the mixture was again agitated for an additional 2 min at high speed. After a total of 5 min conditioning, including addition of the soap and its dispersion,

Table 2

Pulping, Peroxide Treatment, and Flotation Conditions

PULPING	
Pulp consistency	8%
pH	10.5
Temperature	60°C
Time	20 min
PEROXIDE TREATMENT	
Pulp consistency	12%
Sodium silicate or Na-A zeolite	0 to 4%
DTPA	0.5%
Peroxide	0.5-3.0%
Temperature	70°C
Time	0 to 120 min
FLOTATION	
Pulp consistency	0.5%
Collector	0.5%
pH	8.5
Time and temperature	10 min and 45°C

flotation was initiated. During flotation the pulp slurry was agitated at 1200 rpm. The flotation conditions are given in Table 2. After flotation, hand sheets were formed and samples were used to determine reflectivity and lignin degradation kinetics.

Test Methodologies

Fourier transform infrared spectra (FT-IR) of samples were determined on a Perkin-Elmer 2000 instrument. Spectra were recorded in the transmittance mode in the range 500 to 4000 cm^{-1} with 4 cm^{-1} resolution. Pulp samples, both peroxide treated and untreated, were dispersed in a tablet of KBr prepared by grinding 1.5 mg of sample with 100 mg of KBr and compressing the whole mixture into a transparent tablet. The compression time was 2 min and the pressure was 10 MPa. The average of three recordings was used to estimate the peak area.

Reflectivity was measured with a Technibrite Micro B Tc-1 apparatus at 457 nm.

The residual zeolite content, residual ink, and other contaminants present in the pulp before and after peroxide treatment and after flotation were determined by thermogravimetric analysis. Initially, about 20 mg of sample was heated up to 700°C in an inert atmosphere to decompose the cellulose, hemicellulose, lignin, and other decomposable contaminants. Then the sample temperature was brought down to 100°C in an inert atmosphere. Finally, the sample was heated to 900°C in an oxygen atmosphere to determine combustible carbon and the residual zeolite content. A thermogram (TG), by itself, was not sufficient to calculate ink, polymer, and residual zeolite content; therefore, a differential thermogram (DTG) was also obtained to quantify these components.

RESULTS AND DISCUSSION

Chromophore Concentration

FTIR spectra of the pulp samples before and after peroxide treatment were used to determine selected chromophore concentrations. Reflectivity measurements were made at 457 nm on 60 g/m^2 basis weight sheets prepared on a standard British handsheet mold.[14] It is well known that reflectance at 457 nm is not directly suitable to study wood chromophore properties as it depends on a complicated function of light absorption (K) and light scattering (S) parameters.[15] In contrast, it has been established that changes in light transmission in the infra-red region is closely related to the fundamental decolorization mechanism of selected chromophores.[16] For example, changes in conjugated ketones with more than one aromatic ring[17,18] and some quinoid structures (chromophores of potential interest in this study) can be correlated[19] with the change in intensity of the peaks at 1600 cm^{-1} and 1647 cm^{-1}. In a mechanical wood pulp containing more than 50% cellulose, the cellulose can be characterized by several low, medium, and high intensity bands. The peroxide treatment conditions used in this study for chromophore modification would not be expected to substantially affect the cellulose.spectrum. Thus, any changes in chromophore concentrations in the peroxide treatment process could be quantified relative to a characteristic peak for cellulose. In the region 980 to 1500 cm^{-1} the carbohydrate spectra are very complicated. Therefore, we selected two ranges of band intensities. The first one extended from 1705 to 1545 cm^{-1} and was assigned to lignin chromophores that reacted with peroxide. The second one, at 896 cm^{-1} and assigned to the antisymmetric out-of-phase C-H stretching in cellulose, was used as a reference to determine the relative concentration of chromophores being eliminated. Examples of the spectra are given in Figure 2. The chromophore concentration was expressed as the ratio of the height of the absorption peak extending from 1705 to 1545 cm^{-1}, corresponding to quinones and ketones with more than one aromatic ring, to the height of the absorption peak at 896 cm^{-1}, corresponding to the C-H band in cellulose. Peak heights were calculated relative to the baselines similar to the procedure used by Sarkanen et al.[20, 21] This ratio or relative IR absorption is designated A_r, where $A_r = [A_{1705-1545}]/[A_{896}]$. The method is illustrated in Figure 3.

A toner-printed, secondary fiber furnish containing 50% TMP newsprint and 50% bleached chemical pulp was treated with peroxide for different time intervals. Figure 4 shows the changes in the reflectance of blue light at 457 nm and the relative IR absorption, A_r. The peroxide treatment increased the reflectivity rapidly during the first 15 min, then more slowly after that. Decreases in the A_r followed a similar trend. However, the initial slope in the latter case was marginally less than that obtained by reflectance. This difference can be attributed to two factors. First, the IR measurement is predominantly influenced by changes in quinoid and α-carbonyl structures.[19] However, it is possible that α-carbonyl compounds do not contribute to the reflectance data at 457 nm whereas some

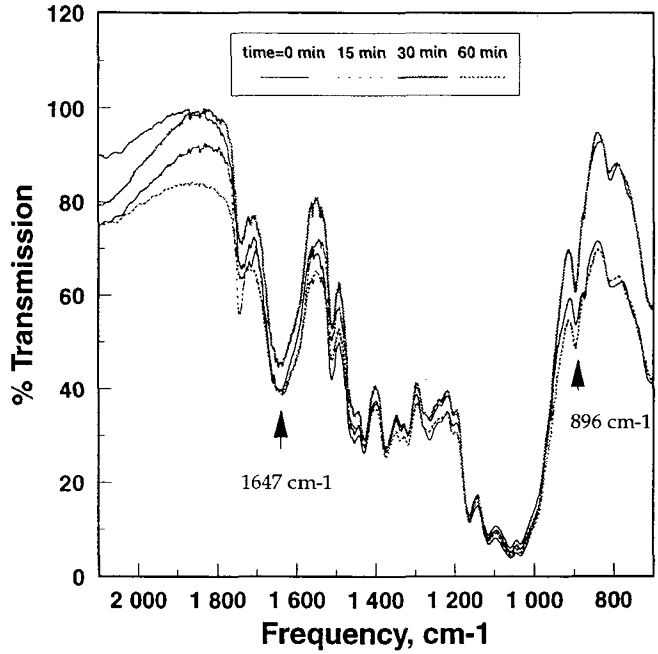


Figure 2. FTIR Spectra of waste wood pulp during peroxide treatment as a function of reaction time.

other colored chromophores which are not considered in our chromophore quantification process do absorb light at 457 nm.[22] Second, the reflectance data is influenced by light scattering as well as absorption. It is known that increases in scattering improve reflectivity and any factor which improves surface smoothness increases scattering. If this is true, a recycled wood pulp containing a significant amount of polymeric residue would experience a gain in its scattering coefficient and the corresponding gain in reflectivity would not truly represent a chromophore elimination effect. Apparently, A_r values of peroxide-treated pulp indicate that the IR data in the selected wavelength range can be used more precisely to study the rate and extent of removal of quinones and α-carbonyl compounds. This

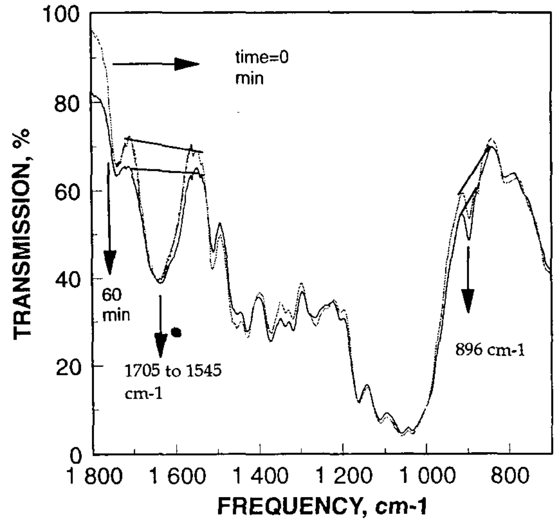


Figure 3. FTIR spectra of secondary fiber from wood pulp showing the frequency bands used for chromophore identification.

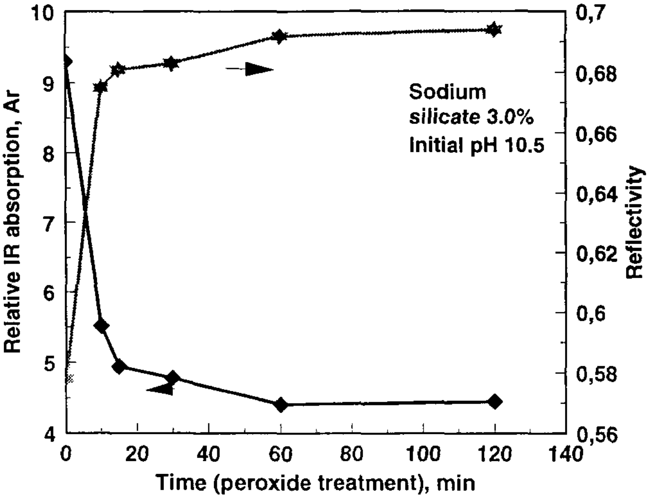


Figure 4. Time changes in the reflectance and relative IR absorption during peroxide treatment.

experimental evidence encouraged us to use A_r data for an indirect determination of selected chromophore concentrations.

Effect of Silicate and Magnesium Sulfate

The effect of sodium silicate and magnesium sulfate on the kinetics of chromophore elimination from ground wood by peroxide has been investigated previously.[14] The general conclusion was that magnesium sulfate did not influence the kinetics of chromophore elimination and sodium silicate acted as a buffer during reaction of the lignin chromophore with peroxide.[5] Our experimental findings on waste wood pulp in the presence of DTPA confirmed that magnesium sulfate did not influence the kinetics of peroxide reaction with quinoid structures and α-carbonyl compounds. The results are shown in Table 3.

Unlike $MgSO_4$, Na_2SiO_3 did have some influence on the chromophore elimination reactions. The change in absorption rate was about 10% relative to unstabilized peroxide brightening. A similar magnitude of change in the absorption coefficient (Kubelka-Munk) at 457 nm with the addition of sodium silicate had been reported by Lundqivst[14] for her study on lignin chromophore reactions in a liquor containing groundwood and hydrogen peroxide.

Effect of Na-A Zeolite

Preliminary experiments were carried out to determine the effect of Na-A zeolite on the chromophore elimination process. Zeolite and/or DTPA was added to the 5% consistency fibrous suspension and then peroxide and caustic were added to start the reaction at a predetermined initial pH. Table 4 shows the pH profile; the chromophore concentration, as measured by IR absorption; and the pulp reflectivity at 457 nm as a function of time without zeolite. Table 5 shows the same type of data for a reaction with zeolite. Sample to sample variation in the pH for two repetitive measurements was 0.1.

Table 3

Effect of Na_2SiO_3 and $MgSO_4$

Reaction time, min	$\Delta A_r/\Delta t$ (min-1)	Na_2SiO_3*	$MgSO_4$*	DTPA*
10	0.41± 0.008	p	p	p
10	0.40± 0.007	p	a	p
10	0.36± 0.010	a	a	p
30	0.16± 0.002	p	p	p
30	0.16± 0.010	p	a	p
30	0.14± 0.009	p	a	a

*p: present; a: absent.

Table 4

pH Profile of Chromophore Reactions without Zeolite

Reaction time, min	pH	Reflectivity (457 nm)*	ΔR	A_r (IR)*	ΔA_r
0	10.8	0.583	0.00	9.41	0.00
30	9.7	0.618	0.035	7.47	1.94
60	9.3	0.623	0.04	7.38	2.03
120	9.1	0.625	0.042	7.29	2.12

*Standard deviation (SD): reflectivity, ± 0.004; A_r, ± 0.021; ΔR and ΔA_r are changes in reflectivity and IR absorbency, respectively.

Table 5

pH Profile of Chromophore Reactions with Zeolite*

Reaction time, min	pH	Reflectivity	ΔR	A_r	ΔA_r
0	10.5	0.575	0.00	9.52	0.00
30	9.6	0.615	0.04	7.58	1.94
60	9.4	0.637	0.062	6.49	3.03
120	9.2	0.646	0.071	6.15	3.37

*4% by weight of Na-A zeolite. SD are the same as in Table 4.

A comparison of the reflectivity and A_r values in Tables 4 and 5 reveals that the chromophore reaction with hydrogen peroxide is positively influenced by the presence of zeolite. It is obvious that a direct addition of DTPA during the peroxide treatment of the pulp is not effective enough to deactivate a significant amount of the metal ions present in the pulp. It is known that Na-A zeolite has good ion exchange capacity. Therefore, it is possible that addition of Na-A zeolite to the reaction system would help to deactivate harmful metals.[23] A patent by Leonhardt *et al.*[24] reported that zeolite can act as a metal deactivator in TMP bleaching. In chromophore elimination reactions from lignin, iron and manganese are the principal metal impurities; copper and other metals are usually present in much lower concentration. Therefore, at least one role of Na-A zeolite in peroxide stabilization may be deactivation of some transition metals. However, insolubility of zeolite in a pulp suspension precludes the ability of this inorganic to be involved in exchange reaction with heavy metals inside the pulp matrix.

Another potential way that the zeolite could deactivate metals in the hydrogen peroxide reaction is through the formation of stable complexes with the transition metals. It is difficult to prove the existence of zeolite-transition metal complexes in the reaction medium because of their low concentration. We examined the effect of the order of addition of sodium hydroxide and Na-A zeolite on the chromophore elimination reaction. Table 6 shows that the final reflectivity value for the system where zeolite was added to the waste pulp prior to NaOH was somewhat higher than for the case where the zeolite was added after the NaOH. However, the reflectivity change was not significant enough to propose that the point of addition of zeolite had an effect. The experimental error in the reflectivity measurements never exceeded ±0.005, which conforms well to experimental error reported in the literature for similar measurements.[14]

Figure 5 illustrates the changes in pH with reaction time with or without zeolite. The initial alkali dosage was the same in the two cases. In the presence of

Table 6

Effect of the Order of Addition of Zeolite*

Order of Addition	Initial pH	Reflectivity	Peroxide Consumed,%
Pulp/Zeolite/NaOH	10.5	0.646	92.8
Pulp/NaOH/Zeolite	10.8	0.632	95.1

*pH and peroxide concentration measurement precision were ± 0.02 and ± 0.5%, respectively.

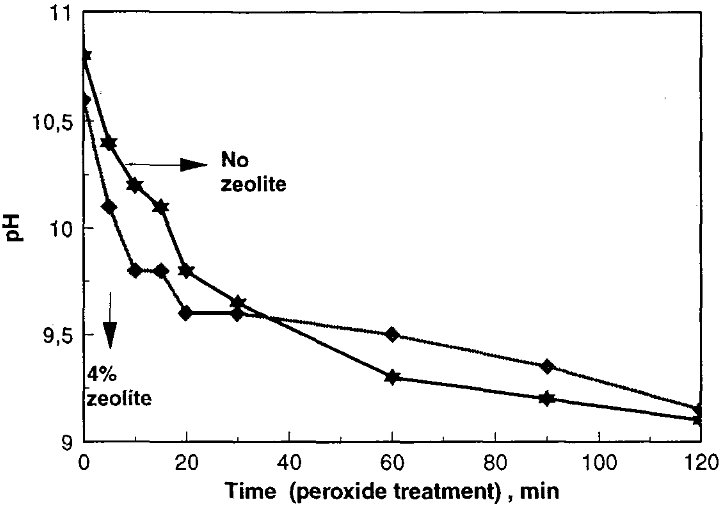


Figure 5. Change in pH as a function of peroxide treatment time with or without Na-A zeolite.

zeolite the pH was initially lower, and did not fall as rapidly as in the absence of zeolite with reaction time, i.e., the pH was maintained above 9.5 for a longer period of time during brightening reaction with zeolite. The precision in pH measurement was ±0.05.

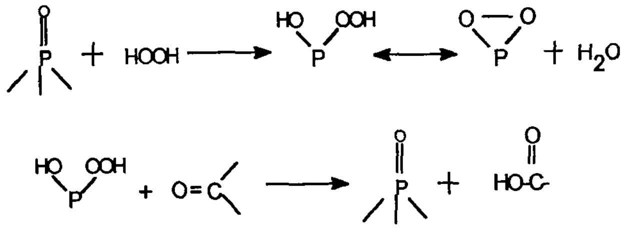
Mechanistic Consideration

Two possible mechanisms are being proposed to explain the improved colored chromophore elimination by peroxide in presence of the treated-zeolite. First, phosphoric acid treated zeolite can form sodium phosphates as discussed earlier in this report. Sodium phosphate containing more than one phosphorous atom in a single molecule, as in sodium pyrophosphate and sodium tri- or tetrapolyphosphate can also be present in the phosphoric acid-treated zeolite cage. It is well known that these phosphates are very good metal chelants and complexing agents, even for heavy metal.[28] Thus, the improved chromophore elimination by peroxide in the presence of treated-zeolite can be attributed to increased metal deactivation by formation of stable metal complexes.

In another possible mechanism, the formation of a phosphoniumperoxo compounds could result from chemisorption of hydrogen peroxide on phosphonyl (P=O) groups.[29-31] These complexes could then oxidize quinoid structures and/or conjugated ketones as speculated in Scheme II.

Practical Significance

This study has shown that chromophores in zeolite-treated secondary fiber from wood pulp respond to peroxide in roughly the same manner as those in sodium silicate-treated secondary fiber. Under similar reaction conditions, zeolite and sodium silicate do, however, have different rates and extents of chromophore removal. Table 7 shows that a 120 min peroxide treatment of repulped fiber with modified zeolite at pH 10.5 and 70°C reduced the relative IR absorption in the 1705-1545 cm^{-1} range (A_r) by about 4.2 points versus 2.0 points without zeolite. Thus, chromophore elimination with zeolite was about twice what it was without the zeolite. However, it is important to point out that chromophore elimination with sodium silicate-stabilized peroxide was better than with zeolite addition. A similar trend was found for reflectivity values.



Scheme II

Table 7

Changes in Optical Properties After Peroxide Treatment (70°C, 120 min)

TREATMENT	PROPERTIES*		CHANGE AFTER TREATMENT	
	Reflectivity	A_r	ΔReflectivity	ΔA_r
Peroxide (3%)	0.627	7.29	+0.047	-2.02
Peroxide + 3% Silicate	0.694	4.45	+0.114	-5.12
Peroxide + 4% Zeolite	0.646	6.15	+0.066	-3.41
Peroxide + 4% Mod. Zeolite	0.672	5.32	+0.092	-4.20

*SD are the same as in Table 4.

Relatively good chromophore elimination in wood pulp secondary fiber by peroxide in conjunction with modified zeolite indicates the potential importance of this type of system in brightening secondary fiber. Laboratory experiments have shown that with a peroxide/modified zeolite treatment of secondary fiber prior to ink separation process, the zeolite can be separated by the flotation process and the zeolite will promotes separation of adsorbed surfactant and polymeric binders from the water effluent. The TGA thermograms in Figure 6 illustrate the efficiency of zeolite separation following the peroxide treatment and flotation deinking sequence of the secondary fiber. The residual zeolite is very small in the treated pulp. This is an advantage over using sodium silicate which tends to deposit on the fiber surface with changing temperature.[31]

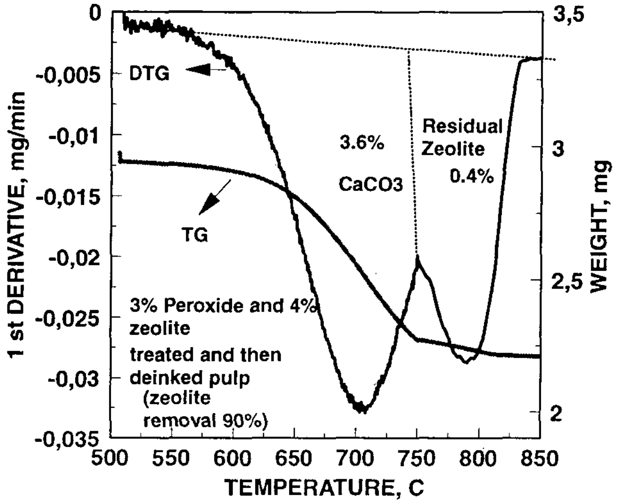


Figure 6. Thermogravimetric (TG) and differential thermogravimetric (DTG) thermograms for secondary fiber pulp after peroxide treatment and flotation showing residual zeolite.

SUMMARY

The elimination of chromophores from wood pulp secondary fibers with peroxide in presence or absence of zeolite has been followed as a function of time by observing the IR absorptivity in the 1545-1705 cm^{-1} range. The zeolite promotes chromophore elimination by peroxide treatment even in absence of sodium silicate. The elimination of chromophores was even more effective if a phosphoric acid–treated zeolite was used with the peroxide. The improved reactivity of peroxide with fiber chromophores in presence of phosphoric acid–treated zeolite may be the result of metal sequestration and/or actual oxidation of the chromophores by phosphoniumperoxo compounds formed in the zeolite.

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