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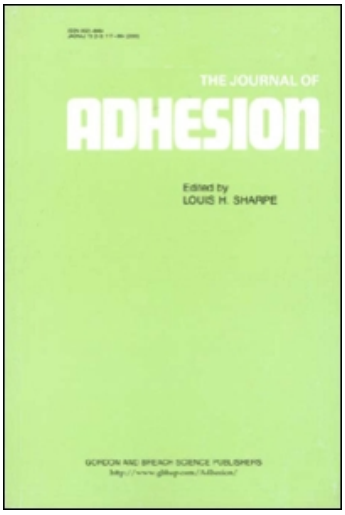

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Bond Formation by Wood Surface Reactions Part II. Chemical Mechanisms of Nitric Acid Activation

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To cite this Article Rammon, R. M. , Kelley, S. S. , Young, R. A. and Gillespie, R. H.(1982) 'Bond Formation by Wood Surface Reactions Part II. Chemical Mechanisms of Nitric Acid Activation', The Journal of Adhesion, 14: 3, 257 — 282
To link to this Article: DOI: 10.1080/00218468208073207
URL: http://dx.doi.org/10.1080/00218468208073207

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J. Adhesion, 1982, Vol. 14, pp. 257–282
0021–8464/82/1404–0257 $06.50/0
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Printed in Great Britain

Bond Formation by Wood Surface Reactions

Part II. Chemical Mechanisms of Nitric Acid Activation

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(*Received November 4, 1981; in final form March 15, 1982*)

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Previous research on chemical bonding has shown that a wood bond can be achieved by surface reactions when the wood is chemically activated prior to pressing. Activation by nitric acid appears to produce the most consistent results. The objective of this study was to elucidate the chemical mechanisms of nitric acid activation through the use of analytical instrumental techniques and identification of wood degradation products. Infrared and ultra-violet spectroscopic analysis of nitric acid treated sugar maple and isolated wood polymers indicated extensive oxidation, nitration and hydrolysis of the wood polysaccharides and lignin. The major effects were noted at ambient temperature although additional treatment at 100°C caused further modification. The lignin and xylan (hemicellulose) were the most extensively modified components as monitored by Klason lignin, Kjeldahl nitrogen and sugar analyses. Lignin is heavily nitrated and over 30% of the xylan (xylose) is lost during nitric acid treatment. The major degradation product isolated from nitric acid treated maple was 2,4-dinitroguaiacol. These findings suggest that oxidation, nitration and hydrolysis of wood polymers are important aspects of nitric acid activation of wood surfaces.

INTRODUCTION

The increased demand for wood products and the dwindling supply of forest resources has increased the need for structural wood composites. The

Presented at the First Annual International Symposium on Adhesion and Adhesives for Structural Materials, Washington State University, Pullman, WA 99164, U.S.A., Sept. 29–Oct. 1, 1981.

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manufacture of wood composite products requires a strong, durable, water resistant adhesive. Phenol-formaldehyde resins are the primary adhesive used today to meet these requirements. These phenolic resins are produced from phenol which is a petroleum derivative. In recent years the increased cost of petroleum has caused much concern about the price of traditional petrochemical adhesives. Figure 1 depicts the trend in phenol prices for the past 15 years, and shows that phenol prices doubled during the period of 1974 to 1976.[1] This tremendous rise in prices for petrochemically based wood adhesives has encouraged research on renewable wood adhesive systems.

Among the renewable wood bonding systems are those that utilize materials derived from wood or the tree. The use of pulping liquors containing lignin has been given a good deal of attention.[2,3] Another category of materials from the tree are the natural polyphenols or tannins. Tannins have long been known to act as extenders for the production of water resistant wood adhesives.[4]

A novel approach to wood bonding involves bonding without adhesives by chemically activating the wood surfaces. A number of activating chemicals have been used successfully to induce chemical bonding.[5–10] Although the

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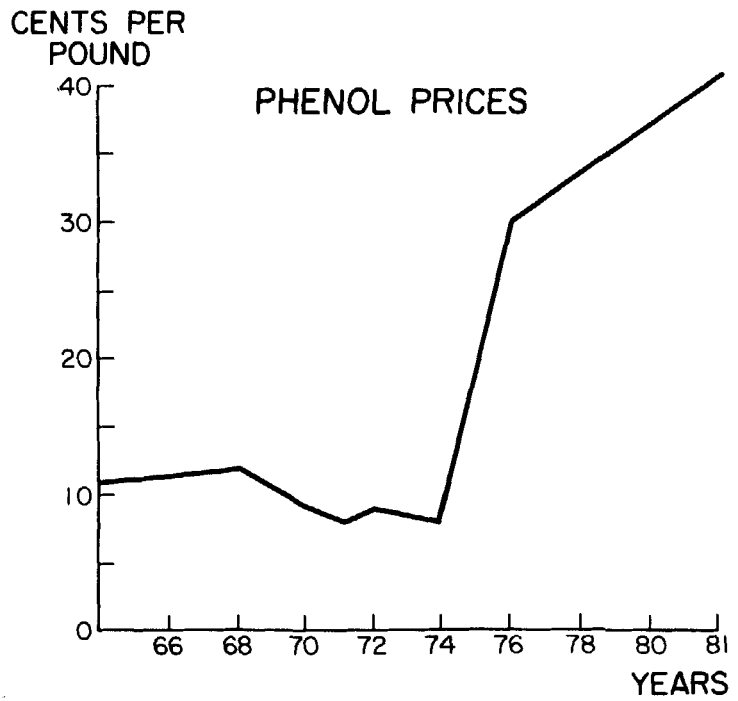

FIGURE 1 Trends in phenol prices.

nature of the reactions produced by these chemical activators has not been fully characterized, a broad classification can be made as to the possible modes of activation based on the chemical nature of the activating agents. The possible modes of activation are:

1. Oxidation (*i.e.*, nitric acid, hydrogen peroxide, etc.)
2. Free radical generation (*i.e.*, ferric ion and hydrogen peroxide)
3. Acid condensation of lignin (*i.e.*, sulfuric acid)

Based on the nature of the activating agents employed, oxidation has been regarded as a major factor in surface activation.[5] The nature of the oxidation as well as other chemical reactions, such as hydrolysis or condensation of the wood polymers have yet to be explored. The objective of this investigation was to ascertain the nature of the chemical changes taking place at the surface of wood during activation and subsequent bonding. A variety of analytical instrumental techniques were utilized and wood degradation products were isolated and identified. In order to facilitate the evaluation of the chemical reactions with wood, the three major wood polymers were isolated from wood, treated with the activating agent and examined by chemical and instrumental techniques. By these means, an evaluation was made of the principal modes of activation and the types of functional groups produced.

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EXPERIMENTAL

The substrates included whole wood, extractive-free wood, isolated wood polymers and model compounds, specifically:

Wood—Wood samples were obtained by finely milling (80 mesh) sugar maple (*Acer saccharum*, Marsh.) in a Micro Mill. The extractive-free wood was obtained by Soxhlet extraction of the wood meal according to ASTM D-1105.[11]

Wood components—Representative wood polysaccharides were alpha-cellulose (Sigma Chemical) and isolated birch acetyl-4-O-methylglucurono-xylan. The isolated lignin substrates were spruce milled wood lignin (MWL) and Orzan (Ammonium Lignosulfonate-Crown Zellerbach Corp.).

Model compounds—A number of model compounds were employed in various instances and are referred to in the text. All of the models utilized were obtained from Aldrich Chemical Company with the exception of cellulose nitrate which was synthesized by the method of Browning.[12]

The chemical treatments were chosen from those known to produce sufficient activation for subsequent bond formation. Activation by nitric acid was the

primary treatment of interest in this study. A variety of other treatments were also used to distinguish between the effect of oxidation and the acid effects of hydrolysis and condensation. The chemical treatments can be roughly classified as follows:

	Oxidation	Acid effects
nitric acid (40%)	X	X
sodium periodate (0.3M)	X	
sulfuric acid (1N)		X
hydrogen peroxide (30%)	X	

The treatment procedure for isolated wood components and wood flakes involved mixing the substrate, in powder form, with a sufficient quantity of chemical activator to moisten the sample completely. This normally resulted in approximately a 1 : 1 ratio by weight. After mixing with the activator, one-half of the sample was allowed to air dry at ambient temperature for 24 h. The remaining half of each mixture was subjected to additional treatment to simulate heating during the pressing cycle of the bonding procedure. This consisted of placing the sample mixture between preheated glass slides in an oven at 100°C for specified lengths of time. The treated samples were stored in a vacuum desiccator until analyzed.

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Instrumental techniques

Infrared spectroscopy The infrared (IR) spectrographs were obtained using a Perkin-Elmer Model 467 grating infrared spectrophotometer. All samples were analyzed in solid form utilizing KBr disks. The KBr disks were prepared using a ratio of 200 mg KBr to 1 mg of sample. For quantitative determination of carbonyl content, the method of "relative absorbance" described by Sarkanen *et al.*[13] was employed. With this technique the absorbance values are computed relative to the absorption of an internal reference band. For lignin, these investigators used the aromatic skeletal vibration at 1500 cm^{-1}. In the determination of carbonyl intensities in cellulose, the C—H out-of-plane bending vibration in cellulose and xylan at 900 cm^{-1} was used as the internal reference.

Ultraviolet spectroscopy The ultraviolet (UV) spectra were obtained utilizing a Beckman Acta III double beam UV spectrophotometer. A methylcellosolve solvent was used for the UV analysis of MWL samples as follows:

1. 12.5 mg of MWL were dissolved in 7.5 ml of methyl-cellosolve and diluted to 25 ml with 95% ethanol (conc. 0.5 mg/ml).

neutral solution 2. 10 ml of solution 1 were diluted to 25 ml with 95% ethanol (conc. 0.2 mg/ml).

alkaline solution 3. 10 ml of solution 1 plus 2.5 ml of 1 N NaOH were diluted to 25 ml with distilled water (conc. 0.2 mg/ml).

The neutral and alkaline solutions were used to obtain the UV ionization spectra. A solvent blank for non-difference spectra was obtained by following the same procedures but without the MWL. All spectra were recorded with sample and reference in matched 1 cm path length silica cells.

Chemical analysis

Wood preparation Unextracted maple flakes were treated with nitric acid (40%) and heated between glass plates as previously described. Three sets of flakes, control (no treatment), acid treated and air dried, and acid treated and heated, were ground in a Wiley mill until they passed a 40 mesh screen. The wood meal was then subjected to quantitative sequential extraction according to ASTM D-1105. The extraction thimbles were oven dried and weighed after each extraction while the extract was dried under vacuum at low temperature before weighing.

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Analytical procedures The Klason lignin, total carbohydrate and sugar content and Kjeldahl nitrogen were determined by established procedures. The Klason lignin analysis was carried out according to the procedures developed by Effland.[14] The content of individual sugars was determined by paper chromatography and corrected for hydrolysis losses. Total carbohydrate content was not corrected for the hydrolysis losses. The Kjeldahl nitrogen procedure was that of the Association of Official Analytical Chemists.[15]

Wood degradation products

The fractionation of degradation products, from the reaction of nitric acid on wood, was accomplished by solvent extraction. The products were isolated into three fractions (acid, phenols and neutrals) on the basis of their partition coefficients in aqueous solvents versus organic solvents at several different pHs.

After methylation with diazomethane the acid fraction was separated into individual compounds by thin layer chromatography (TLC). The TLC was done on Whatman TLC preparative plates precoated with silica gel. The chromatograph was developed by elution with chloroform. The separated compounds were recovered from the silica gel and characterized by IR, proton nuclear magnetic resonance (NMR) and mass spectroscopy (MS) techniques.

RESULTS AND DISCUSSION

The aim of this study was to monitor the chemical changes occurring during activation of wood surfaces and subsequent bond formation. A generalized procedure for bonding involves treating the wood surfaces with the chemical activator and allowing them to air dry. After a period of drying the surfaces are remoistened with water and pressed together at elevated temperatures forming a bond between the adjacent wood surfaces.[5-10] Of particular interest are the effects of the open drying period and the heating on the activation of the wood. Although a number of different activating agents have been employed for chemical bonding, nitric acid has produced the strongest bonds.[5,16] In this investigation, the effect of nitric acid as an activating agent was inferred from analyses of isolated wood components and whole wood treated under similar conditions.

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Analysis of carbohydrate components

The carbohydrate fraction of wood is comprised mainly of cellulose and the hemicelluloses. These two components, referred to collectively as holocellulose, represent approximately 70% of the dry weight of wood. Of this, about 2/3 is the polysaccharide cellulose. The IR spectra of polysaccharides are generally quite diffuse in nature, so that spectral changes are not always well defined. It is convenient, therefore, also to use the disaccharide, cellobiose, as a model of cellulose reactions.

Treatment of cellobiose with nitric acid at ambient temperature resulted in a slight increase in absorption in the carbonyl region (1735 cm^{-1}) and reaction at 100°C produced a large increase in this region. The treatment of cellulose with nitric acid gave results similar to those obtained with cellobiose. The ambient temperature treatment exhibited a slight carbonyl absorption at 1735 cm^{-1}, while the 100°C reaction gave a much stronger peak (Figure 2). The occurrence of a carbonyl absorption band in cellulose can be attributed to oxidation of one or more of the hydroxyl groups. To determine the nature of this oxidation, comparisons were made with other oxidizing agents.

The oxidation of cellulose by periodate is a well known reaction. The mechanism involves cleavage of the pyranose ring and production of aldehyde groups at C2 and C3. This product, which has been referred to as dialdehydocellulose,[17] should result in an absorption in the carbonyl region of the IR spectrum. The IR spectra, however, does not exhibit absorption in the carbonyl region neither after ambient temperature treatment nor from the 100°C reaction. This lack of absorption is probably due to either formation of hemiacetal bonds or hydration of the aldehyde groups.[17]

The oxidation of cellulose by hydrogen peroxide parallels the results

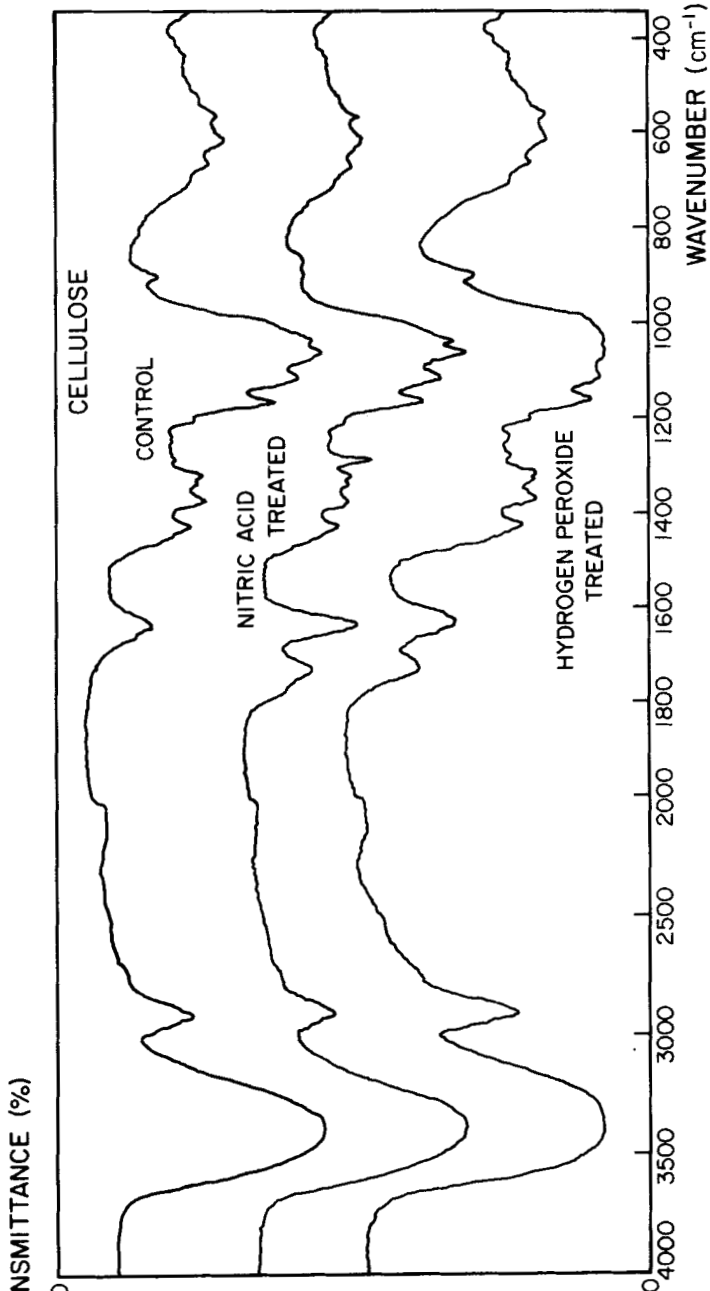

FIGURE 2 IR spectra of cellulose and oxidized cellulose.

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obtained with the nitric acid treatment. At ambient temperature little oxidation is achieved, but reaction at 100°C produces a strong absorption at 1735 cm^{-1}, as shown in Figure 2. With both oxidants (nitric acid and hydrogen peroxide) the primary alcohol group at C6 is the most probable site for oxidation to occur. Primary alcohols are oxidized to aldehydes which are even more rapidly oxidized to carboxyl groups to yield carboxycellulose.[17,18] The fact that the oxidation goes completely to the carboxylic acid can be demonstrated by the shift in absorption which occurs on salt formation. Exposure of both the nitric acid and peroxide oxidized samples to ammonia vapor for 15 minutes results in a shift of the 1735 cm^{-1} band to approximately 1600 cm^{-1} (Figure 3). This is indicative of the formation of the corresponding salt of the acid.[17,19] The shift is complete for the peroxide oxidized sample and nearly so for the nitric acid treated sample. The sample oxidized by nitric acid continues to show a slight residual absorption in the carbonyl region after exposure to the ammonia. This is presumably due to a small percentage of aldehyde or ketone groups from the nitric acid oxidation, which was also indicated in a previous analysis of nitric acid activation by ESCA.[5]

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Further examination of the IR spectra of nitric acid treated cellulose indicates that in addition to oxidation there is some evidence of nitration of the cellulose as well. The nitration is indicated by the absorptions at 1650 cm^{-1}, 1280 cm^{-1} and 850 cm^{-1} which can be assigned to nitric ester groups.[17,19]

In addition to the nitrate ester absorption, the ambient temperature treatment yields a very strong absorption band at 1385 cm^{-1}. This peak has been assigned to free nitronium ions (NO^+) in both IR and Raman spectra.[17] The nitronium ions, which are reactive as both a nitrating and an oxidizing agent, are due to unreacted nitric acid absorbed by the cellulose. This absorbed acid may be regarded as reserve oxidizing agent, which reacts upon heating during the pressing procedure in wood bond formation.

The fate of the absorbed acid as a reserve oxidizing agent was monitored as the sample was heated for different time periods. Thus a sample of cellulose was treated with nitric acid in the normal manner, and allowed to air dry at ambient temperature for 24 h. After drying, the sample was divided into four portions and heated at 100°C for 0, 10, 20, and 30 minutes, respectively. The absorbances at 1385 cm^{-1} and 1735 cm^{-1} were calculated relative to the band at 900 cm^{-1} for each sample. As shown in Figure 4 the absorption at 1385 cm^{-1} decreased with increased time at 100°C, while the carbonyl peak at 1735 cm^{-1} increased in intensity. This demonstrates that even after 24 h at ambient temperature there is still sufficient absorbed acid in the cellulose to produce further oxidation upon heating. Furthermore, the consumption of the reserve oxidizing agent appears to be related to increased oxidation of the cellulose. This reserve oxidizing agent may be related to the decrease in shear strengths obtained with longer ambient drying periods reported by Young *et al.*[5] One

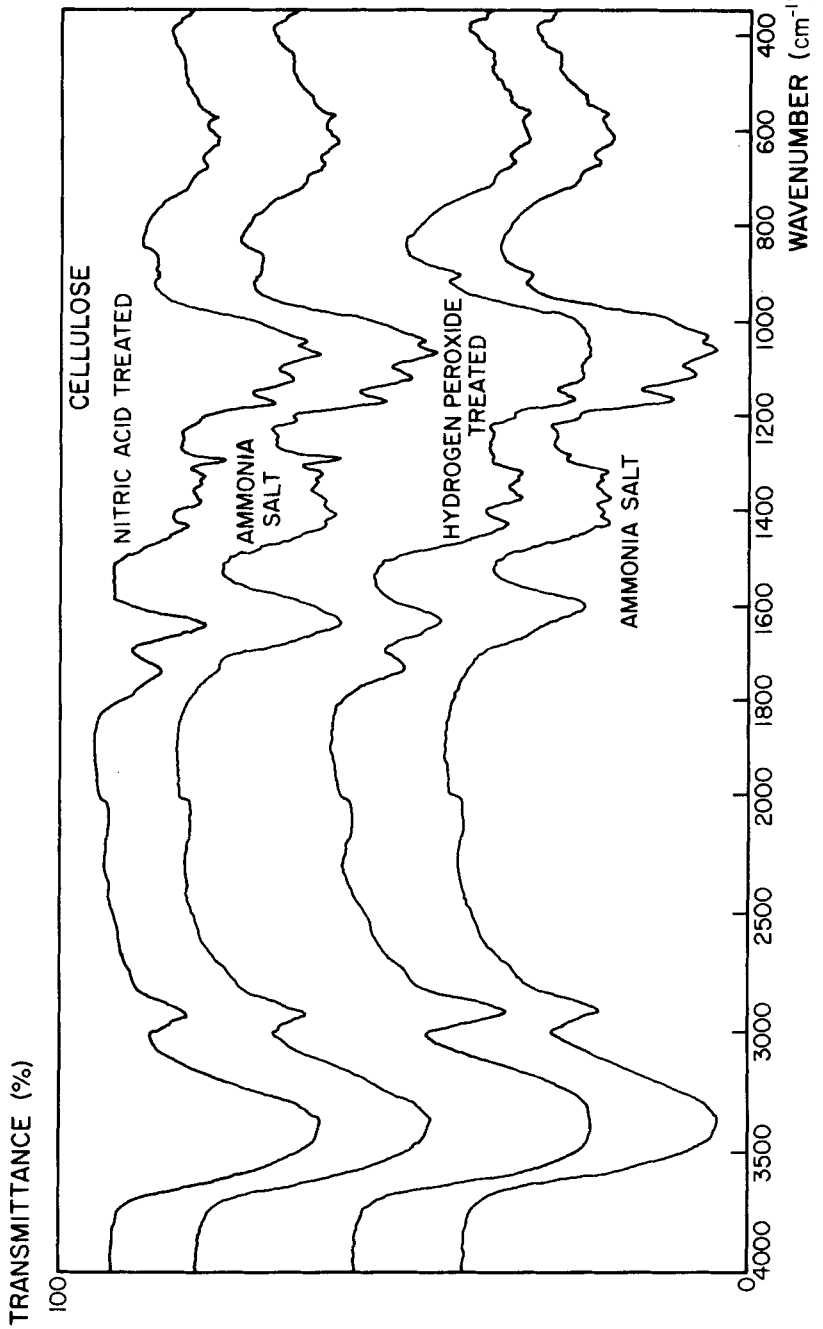

FIGURE 3 IR spectra of oxidized cellulose showing shift with salt formation.

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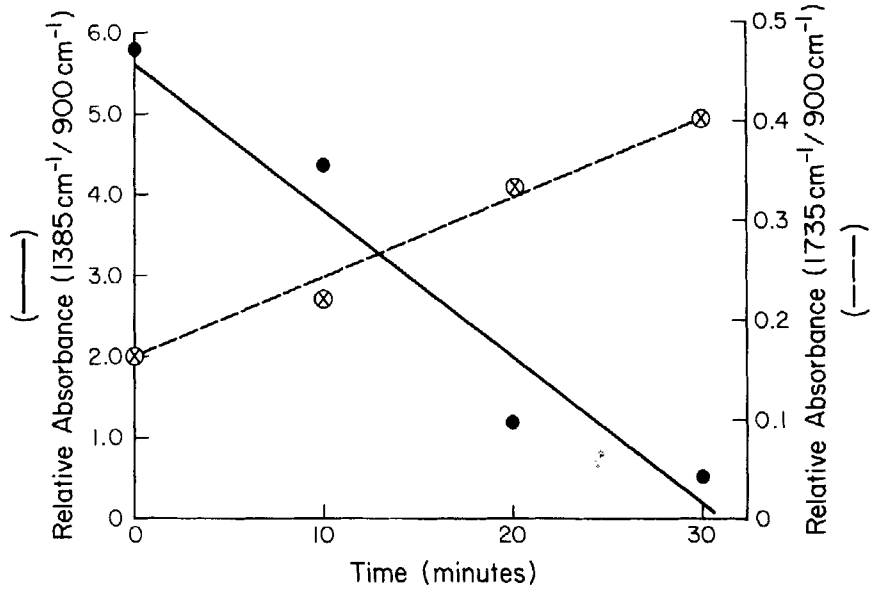

FIGURE 4 Absorbance for cellulose at 1735 cm^{-1} and 1385 cm^{-1} relative to internal reference band at 900 cm^{-1} *v.* time at 100°C; after nitric acid treatment and 24 hour ambient temperature drying period.

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explanation for the loss in strength is that it results from increased acid degradation of the wood substrate after prolonged contact with the nitric acid. Another contributing factor may be the loss of reserve oxidizing agent. At longer drying times one would expect a corresponding loss of absorbed acid, either through vaporization or diffusion away from the surface of the wood, and therefore less oxidation upon heating.

The other major carbohydrates in wood are the hemicelluloses, with xylan the predominate hemicellulose of hardwoods. When the acetyl-4-O-methyl-glucuronoxylan is mixed with nitric acid it is completely dissolved to form a viscous, resin like solution. Upon drying at ambient temperature the xylan solidifies to form a continuous film. Comparing the spectra in Figure 5 before and after treatment at ambient temperature, it appears the major change is a decrease in the carbonyl band. This probably indicates a loss of acetyl groups when the sample is dissolved in the acid. The acetyl groups present in hemicelluloses are readily hydrolyzed by acid to form acetic acid in solution.[12] The decrease in the band at 1250 cm^{-1} can also be ascribed to the loss of acetyl groups.[20] In addition, the glycosidic bonds in the hemicellulose can also be hydrolyzed by acid.

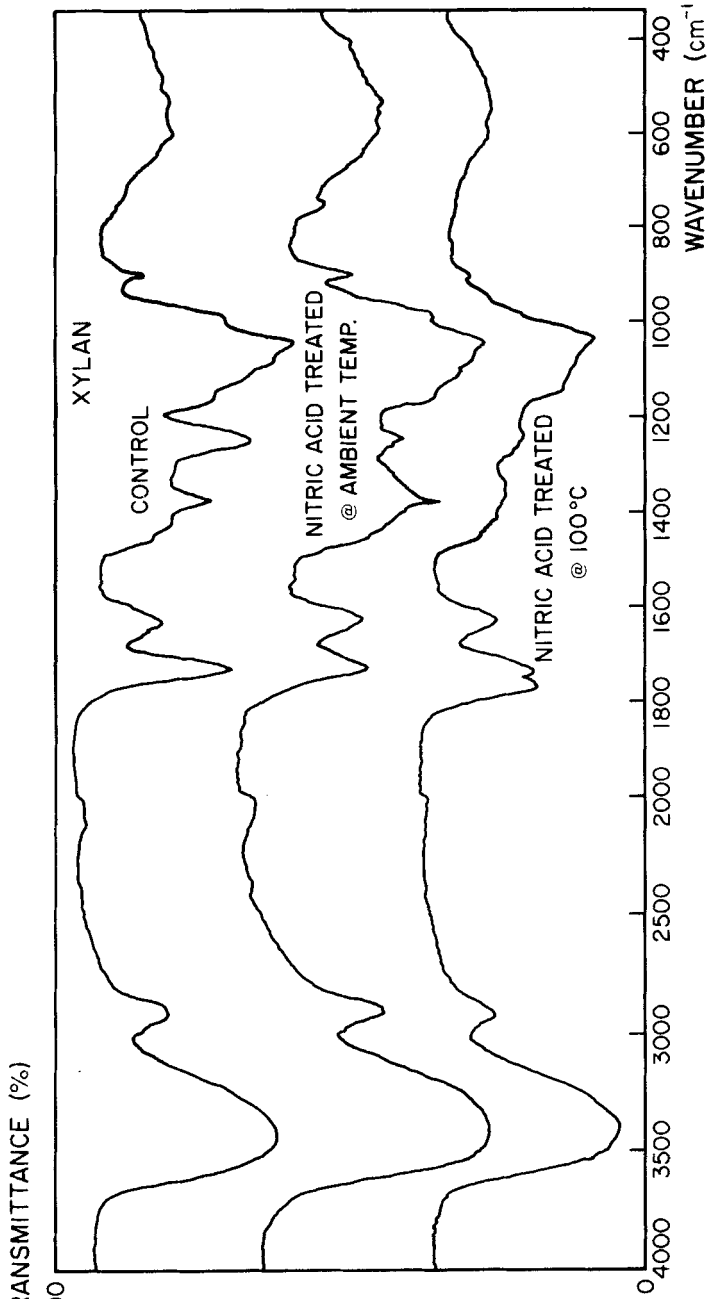

FIGURE 5 IR spectra of xylan before and after nitric acid treatment at ambient temperature and at 100°C.

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At 100°C the xylan is more extensively modified as indicated by the spectra in Figure 5. The more diffuse nature of the spectrum possibly indicates hydrolysis and recondensation of the polysaccharide. In addition to the loss of band resolution, the carbonyl absorption has split to form a doublet. The second absorption peak is at 1775 cm^{-1}. Absorptions in this region are typical of a γ-lactone structure.[19,21] This may be the result of oxidation of the sugar units to uronic or aldonic acids which are generally isolated as their γ-lactones.[22]

The fact that nitric acid treatment of xylan produces a continuous film which upon heating forms a modified product, might suggest that the hemicellulose fraction contributes to bond strength in nitric acid bonding through enhanced plasticization of the bond line. This effect may be similar to improved strength for paper made from high hemicellulose content pulps.[23] The improvement in paper strength attributed to hemicellulose is partly due to increased plasticization of the fibers. The hemicellulose may also degrade under acid conditions to form furan derivatives such as furfural which can polymerize and act as adhesives. The xylan/nitric acid mixture, in fact, when pressed between two pieces of wood forms a strong bond. Although the bond has good strength it is not resistant to water.

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Analysis of the lignin component

Since nitric acid is known to function as a pulping agent, nitric acid activation of wood would be expected to react extensively with the lignin fraction. The mechanism of nitric acid pulping, like all chemical pulping systems, is to degrade the lignin into lower molecular weight soluble products.

Lignin is quite easily oxidized and dilute nitric acid treatments tend to oxidize rather than nitrate the lignin.[24] The IR spectra of milled wood lignin (MWL) treated with nitric acid at ambient temperature showed an increase in the carbonyl region near 1730 cm^{-1} which indicates oxidation. The calculated relative carbonyl absorptions presented in Table I are essentially the same for the ambient temperature treatment as for the 100°C treatment. This would indicate that the oxidation of the lignin is essentially complete during the open drying period and is not dependent upon heating.

While it has been stated that dilute nitric acid tends to oxidize rather than nitrate, the acid concentrations employed for activation are great enough that some nitration of the lignin would be expected. The IR spectra also showed absorptions indicative of substitution of nitro groups on the aromatic ring, at 1340 cm^{-1} and a shoulder at 1580 cm^{-1}.[25] The assignment was confirmed using model compounds. The spectrum of 5-nitrovanillin has absorptions at 1560 cm^{-1} and 1340 cm^{-1} which are not present in the spectrum of vanillin.

TABLE I

Carbonyl absorptions at 1735 cm^{-1} for lignin relative to the absorption at 1500 cm^{-1}†

	Δ Absorbance		Ratio
	A1735 cm^{-1}	A1500 cm^{-1}	A1735/A1500
MWL control	0.124	0.578	0.214
MWL HNO_3 @ amb. T.	0.197	0.173	1.139
MWL HNO_3 @ 100°C	0.126	0.129	0.977
Orzan control	0.031	0.176	0.176
Orzan HNO_3 @ Amb. T.	0.075	0.044	1.700

† The 1500 cm^{-1} absorption is chosen as an internal reference because of its relatively constant intensity.

The same pattern is exhibited for the spectra of 4-hydroxy-3-methoxybenzoic acid and 4-nitro-3-methoxybenzoic acid.

Hydrolysis of lignin linkages and subsequent condensation reactions undoubtedly occur with nitric acid treatment. The IR spectra obtained after nitric acid treatments of MWL and lignosulfonate are more diffuse and less well resolved than the control spectra. This is generally indicative of higher molecular weight products formed by condensation. It appears, however, that condensation reactions are not making a significant contribution to the covalent bonding between the wood surfaces. The carbon to carbon bonds resulting from condensation would be expected to impart more water resistance than has been realized from nitric acid bonding of wood. The spectrum of MWL after the elevated temperature treatment with nitric acid is only slightly more diffuse than after the ambient temperature treatment with the acid. The condensation reactions, therefore, may be occurring on the wood surfaces during the open drying period and would be essentially complete prior to the pressing procedure.

The UV spectra of lignin can be used to further characterize the effect of nitric acid activation. The UV spectra of MWL before and after nitric acid treatment are given in Figure 6a. At first glance it would appear that the nitric acid treatment results in only a loss of the absorption maxima at 280 nm. However, it can be seen in the difference spectrum (Figure 6b) that the apparent loss of the absorption peak is due to a combination of effects. There is a decrease in absorbance at 280 nm, but there is also an increase at 260 nm. This increased absorption at 260 nm tends to fill in the trough which distinguishes the 280 nm maximum from the rest of the spectrum.

There appears to be three major influences of the nitric acid treatment on lignin. The first is the increased absorbance at 260 nm. Pew[26] has established that an increased absorption at 260 nm is due to the presence of biphenyl units.

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This would indicate that the nitric acid treatment results in condensation of lignin units. The decreased absorbance at 280 nm is the second feature of the difference spectrum. The 280 nm maxima has been assigned to the absorption of the aromatic ring in lignin.[27] The decrease in absorption in this region is most likely due to oxidation of the aromatic nuclei to non-aromatic structures such as quinonoids.[28] The third and most distinctive feature of the difference spectra is the large increase in absorption at the high wavelengths (300–400 nm). Strong absorptions in this region have been shown to be most greatly

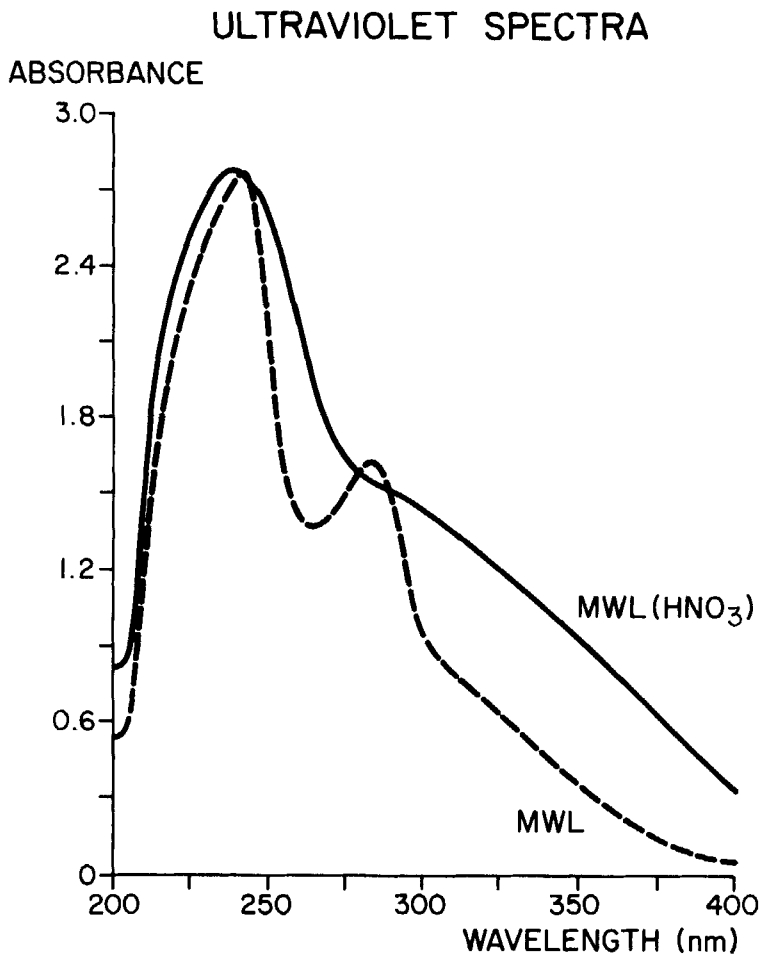

FIGURE 6a UV spectra of MWL before and after nitric acid treatment.

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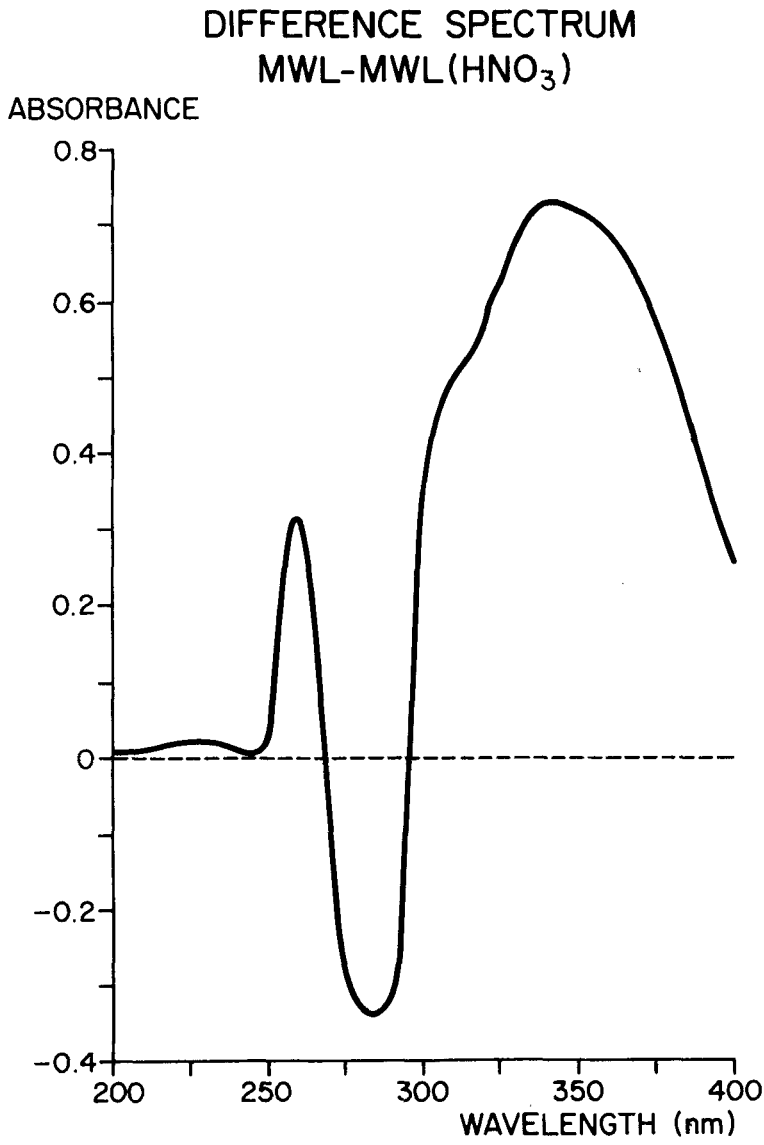

FIGURE 6b UV difference spectra; MWL and MWL after nitric acid treatment.

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affected by the presence of side chain carbonyl groups.[26,29] This indicates that oxidation of the side chain occurs during nitric acid treatment.

The ionization difference curves for MWL and for MWL treated with nitric acid were also recorded (Figure 7). This technique is utilized to detect concentrations of ionizable phenolic hydroxyl groups in lignin samples. The major differences in these spectra are that the nitric acid treated sample does not have an absorption maxima at 300 nm and the high wavelength maxima is shifted to even longer wavelengths than the untreated sample. The maxima at 300 nm is characteristic of non-conjugated phenolic hydroxyls, while the long wavelength absorption is due to conjugated phenolic hydroxyls.[12] This indicates that the nitric acid treated sample is deficient in the non-conjugated free phenolic hydroxyl groups. Lignin units with free phenolic hydroxyls are very susceptible to nitric acid degradation and therefore apparently do not persist after the oxidative treatment. The shift to higher wavelengths indicates that the free phenolic hydroxyls remaining after nitric acid treatment are very highly conjugated. This correlates with the increase in yellow color associated with the nitric acid treated lignin.

The spectroscopic evidence suggests that the lignin portion of wood is extensively modified by nitric acid treatment. This modification appears to include oxidation, nitration, degradation and condensation. The lignin portion of the wood appears to be less dependent on heating to achieve activation than the carbohydrate fraction.

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Examination of whole wood

The insight gained through the spectroscopic investigation of the individual polymer components of wood can be used to characterize the activation of whole wood. The effect of oxidation after nitric acid treatment is evident from the broadening of the carbonyl peak in the IR spectrum of wood (Figure 8). The extent of the oxidation can be determined by calculation of the relative absorbance of the peak at 1735 cm^{-1} to the 1500 cm^{-1} peak. The results presented in Table II show that the oxidation of wood follows the same pattern previously established for cellulose. The ambient temperature treatment has a slight oxidative effect while the 100°C treatment produces the major oxidation reaction. The broadening and increased intensity of the band at 1650 cm^{-1} can be attributed to the formation of nitrate esters on the polysaccharide component. The analysis of the cellulose discussed previously showed this region of the spectrum to be the most highly affected by nitration.

The extraneous portion of wood, which is only a few percent by weight, could also have an effect on the overall activation of wood. The hydrophobic nature of wood surfaces determined by ESCA analysis, indicated that there may be a higher concentration of extractives at the surface.[5] This would allow

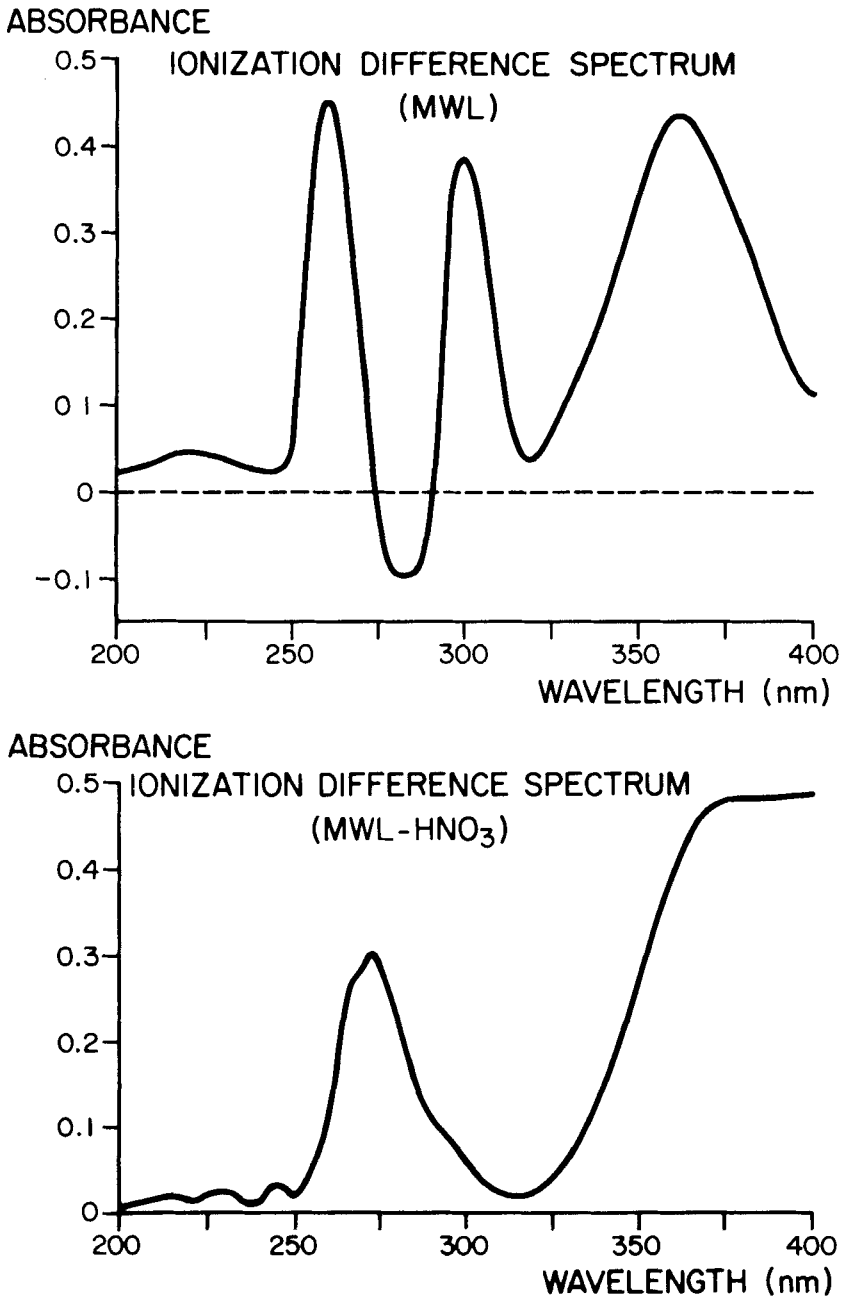

FIGURE 7 Alkaline-neutral difference spectra for MWL and MWL after nitric acid treatment.

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TABLE II

Carbonyl absorptions at 1735 cm^{-1} for wood relative to the absorption at 1500 cm^{-1}

	Δ Absorbance		Ratio
	A1735 cm^{-1}	A1500 cm^{-1}	A1735/A1500
Wood control	0.149	0.062	2.258
Wood HNO_3 @ Amb. T.	0.073	0.062	2.607
Wood HNO_3 @ 100°C	0.141	0.027	5.222

more active participation of extractives in bond formation than their normally low amounts would suggest. The IR analysis of extractive-free wood yields results identical to the unextracted wood. The extractives presumably react with nitric acid the same as the other components in wood, and may play a role in bond formation. Their presence in such small quantities, however, would limit their influence on the IR spectrum of wood.

To summarize the spectroscopic analysis, it appears that the activation of wood by nitric acid is a two-stage process. The first stage, at ambient temperature, is primarily involved with the lignin component. The activation of lignin at ambient temperature involves oxidation, nitration, degradation and condensation. This initial phase also results in some nitration and possibly hydrolysis of the cellulose and hemicelluloses (xylan). The second stage, which is the effect of heating, involves the major oxidation of the cellulose by reserve oxidizing agent. The heating is also responsible for further degradation and modification of the lignin and hemicelluloses. Analysis of wood fractions resulting from the nitric acid treatment of wood, provided further indications of the mechanisms involved in activation.

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Chemical analysis

In an attempt to corroborate the spectral analysis, a chemical analysis of wood flakes subjected to nitric acid treatments was performed. The effect of the different treatments on the amount of Klason lignin and total carbohydrate are shown in Table III. It can be seen that the nitric acid treatment significantly reduced the amount of Klason lignin. The most dramatic decrease in Klason lignin was between the control and the sample treated at room temperature. Heating the nitric acid treated wood caused a smaller but significant decrease in the Klason lignin content of the treated sample. This loss can be accounted for by two similar reactions.

Nitric acid is a good pulping reagent that will nitrate lignin at the number 1 and 5 positions of the aromatic ring.[30,31] The propyl side chain is displaced

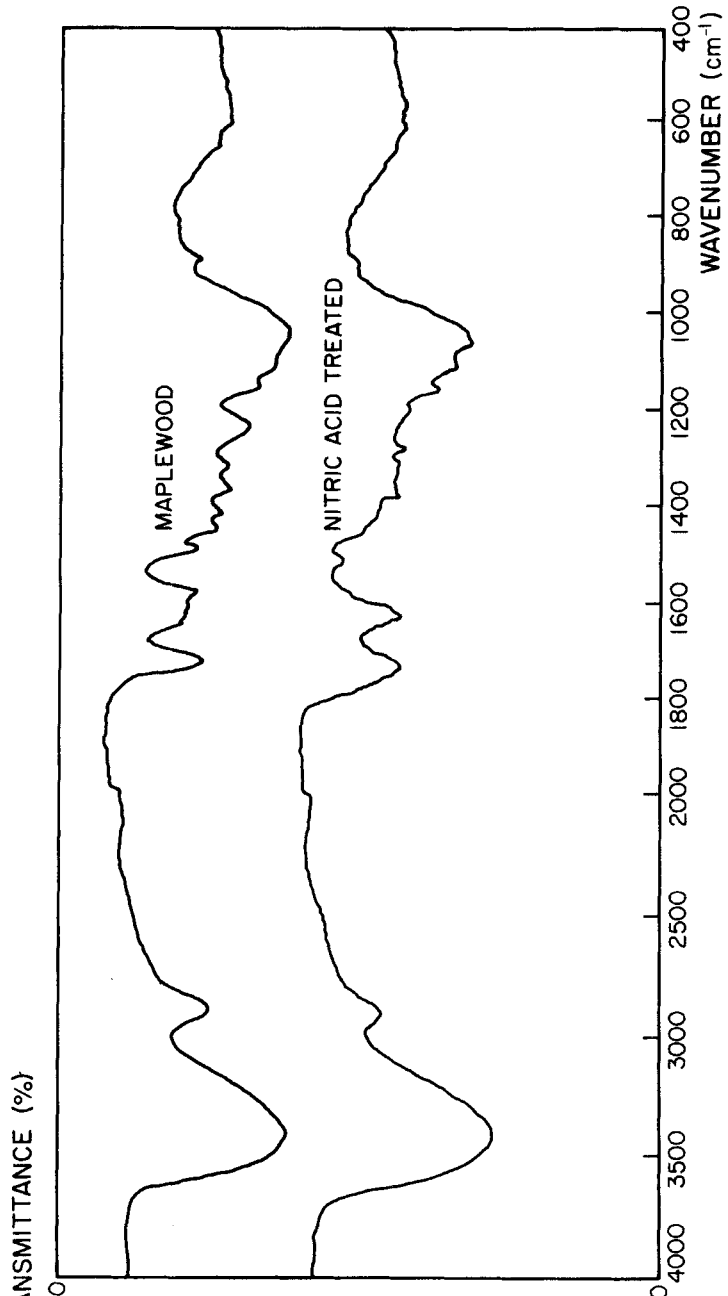

FIGURE 8 IR spectra of whole wood (sugar maple) before and after nitric acid treatment.

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TABLE III

Total carbohydrate and Klason lignin content of sugar maple subjected to different nitric acid treatments

	% Klason lignin[2]	% Total Carbohydrate[1]
Control	22.56	74.49
Treated with 40% nitric acid	7.12	63.45
Treated with 40% nitric acid and heated to 100°C	4.81	63.13

[1] % total carbohydrate is not corrected for hydrolysis losses and corresponds to the total reducing sugar content of the neutralized hydrolyzate.

[2] Accuracy: Klason lignin ±0.3; total carbohydrate ±1.0.

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when the lignin moiety is substituted at the 1-position. Thus the reaction can produce low molecular weight degradation fragments by this and other mechanisms. As a result of nitration of the aromatic rings, condensation reactions are inhibited between rings. This results in lower yields from the Klason lignin analysis since the substituted product is soluble in the sulfuric acid solution. Nitric acid is also known to open up the aromatic ring and form a wide variety of low molecular weight degradation products.[31] These degradation products would also be soluble in the sulfuric acid solution and would not appear as Klason lignin. Thus the dramatic decrease in Klason lignin can be accounted for in two ways; one is the nitration of the lignin moiety which inhibits condensation and the second is loss of the lignin aromatic rings by nitric acid degradation.

The carbohydrate component also exhibited a noticeable reduction after the wood was treated with nitric acid (Table III). Analysis for specific sugars in the carbohydrate fraction showed some significant changes due to nitric acid treatment (Table IV). All the sugars showed a decrease after the nitric acid treatment of the wood at room temperature. The glucose and mannose content were only slightly decreased while the content of xylose, galactose and arabinose was reduced significantly. Except for glucose, all the other sugars are generally associated with the hemicellulose fraction of wood. Glucose, of course, is the main constituent of cellulose but also occurs as a component of the main chain of the glucomannan hemicellulose.[32] Both galactose and arabinose are only minor constituents of hardwood hemicelluloses and their loss or conversion should not be significant to wood bonding.

The large loss of xylose, on the other hand, is very important because this sugar is the main backbone constituent of maple O-acetyl-4-O-methyl-glucuronoxylan.[32] Xylan is by far the predominant hemicellulose in hard-

TABLE IV

Relative amounts of individual sugars after nitric acid treatment and extraction[1]

Treatment	Galactose	Glucose	Mannose	Arabinose	Xylose
Control	1.03	52.07	3.33	1.22	12.60
Treated with 40% nitric acid	0.48	50.77	3.26	0.37	8.57
Treated with 40% nitric acid and heated at 100°C	0.66	50.87	2.75	0.39	8.53

[1] % individual sugars are corrected for hydrolysis losses. Results in % of ovendry wood. Accuracy: total carbohydrate ±1.0; galactose ±0.1; glucose ±1.0; mannose ±0.1; arabinose ±0.2; xylose ±0.01; and nitrogen ±0.02.

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woods representing 20–35% of extractive free wood. The hydrolysis rate of the xylan glycosidic bond is expected to be about 7 times greater than that of cellulose and about 4 times greater than that of mannose based on disaccharide studies.[33] Thus it is not surprising that the xylan is extensively hydrolyzed during the nitric acid treatment.

The heat treatment of the nitric acid treated wood does not significantly further alter the xylose content (Table IV). However the mannose content is reduced a small but significant amount. Based on hydrolysis rates alone we would expect some loss of mannose from the glucomannan hemicellulose. In addition, the hemicelluloses are amorphous polymers which are readily accessible to the action of the acid as compared to the resistant, crystalline cellulose.

The susceptibility of polysaccharide gylcosidic bonds to acids has been known for a long time. Hexoses such as glucose can in turn form 5-hydroxymethylfurfural by further acid dehydration; while pentoses such as xylose can form furfural. It is possible that the loss of xylose was due to conversion to furfural which would be an important component of wood bonding by surface reactions.

Analysis of extracts In an attempt to account for the losses of both lignin and carbohydrate, the material removed by an extraction sequence was quantitatively analyzed. The Soxhlet extraction steps were benzene:ethanol (2:1), ethanol and finally distilled water. The solvent was evaporated *in vacuo* and the residue was dried and weighed. The total weight of residue for each of the extractives is shown in column A of Table V. The Klason lignin content and the carbohydrate content of the residue was also determined and the results are shown in columns B and C of Table V. The amount of "other" material was obtained by difference (A−(B+C)) and represents the non-lignin, non-

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TABLE V

Analysis of extractable material for sugar maple before and after nitric acid treatment

Sample	A. Total extracted material (mg)	B. Klason lignin[2] content (mg)	C. Carbohydrate content (mg)[1]	D. "Other" material A−(B+C) (mg)
Control				
Benzene : ethanol (2 : 1)	39.0	5.38	7.33	26.3
Ethanol	13.0	3.33	1.80	11.2
Water	25.0	18.18	4.57	1.3
Nitric acid treated				
Benzene : ethanol (2 : 1)	343.0	53.30	114.70	175.0
Ethanol	60.0	3.65	28.48	27.9
Water	287.0	31.53	59.57	195.9
Nitric acid treated and heated				
Benzene : ethanol (2 : 1)	384.0	76.80	120.70	176.4
Ethanol	83.8	5.26	25.60	52.9
Water	290.0	47.90	103.00	139.1

[1] % total carbohydrate is not corrected for hydrolysis losses and corresponds to the total reducing sugar content of the neutralized hydrolyzate.
[2] Accuracy: Klason lignin ±0.3; total carbohydrate ±1.0.

carbohydrate fraction of wood. Of course, for untreated wood (control) this simply represents the extractives present. For the sugar maple sample utilized in this investigation the extractives accounted for about 4% of the dry wood (benzene : ethanol extraction).

After treatment with nitric acid there is a dramatic increase in the amount of material extractable with the three solvents (Table V). Both the Klason lignin content and the carbohydrate content in the extracts increased dramatically. A very large increase is noted in the amount of "other" material. This other material probably represents the low molecular weight degradation products from the nitric acid treatment of wood. It has already been shown that nitric acid decreases both the carbohydrate and lignin content of wood. It appears that a considerable fraction of these wood polymers are further converted to lower molecular weight chemicals.

Nitrogen analysis It has already been speculated that the nitric acid treatment causes nitration of the lignin which can significantly affect the Klason lignin determination. Kjeldahl nitrogen analysis of both the Klason lignin and acid soluble lignin showed significant increases in nitrogen as a result of the nitric acid treatment. Most of the nitrogen was retained in the Klason lignin (3.41%) with a smaller amount in the acid soluble lignin (0.3%). Obviously, there is considerable nitration of the lignin aromatic rings taking place. However, the reaction conditions are not so harsh that the nitrated portions are totally removed or totally converted to acid soluble lignin. The specific structure of some lignin degradation products are discussed in the next section.

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Wood degradation products[34]

The degradation products from the nitric acid treatment of wood were obtained by solvent extraction and fractionated into three groups: acid, phenols and neutral fractions. Since the wood was extracted before treatment, the compounds recovered must originate from the reaction of nitric acid on the three major wood polymers, cellulose, hemicellulose and lignin. The acid fraction represented the major portion (78%) of the degradation products isolated. After methylation with diazomethane, the acid fraction was separated into individual compounds by thin layer chromatography (TLC). The mixture separated cleanly into three components. The main component which amounted to 66% of the crude acid fraction was obtained as a pure crystalline compound and subjected to analysis by IR, proton NMR and mass spectroscopy for identification.

The NMR spectrum of this compound indicated that the molecule was aromatic by the presence of two peaks far down field at 8.0 ppm. Two peaks in

the aromatic region indicated two different aromatic protons with a large peak at 4.0 ppm due to methoxy protons. The integration of the signal indicated a ratio of 1 : 1 : 6 for the three different protons. The IR spectra gave indications of nitro groups but not a carbonyl. The combined spectral evidence points to a dinitroguaiacol structure. The mass spectrum obtained from this compound indicated a molecular weight of 228 which confirms the tentative identification made by the NMR and IR. The mass spectra also showed a fragmentation pattern consistent with the proposed structure shown in Figure 9. The isolation of 2-4-dinitroguaiacol has been previously reported in nitric acid pulping studies.[12,30] The probable mechanism of formation of the dinitro compound involves an electrophilic substitution at the 5 position of the aromatic ring of lignin. This is followed by displacement of the side chain and nitration at position 1 of the ring to form the final product (Figure 9).

The second component represented 24% of the crude acid fraction. This compound was also examined analytically for identification by IR, NMR, and mass spectroscopy. Based on the spectroscopic analysis, the molecule appears to have the structure shown in Figure 10. The origin of this compound is more difficult to ascertain; however, based on the position of the methoxyl and nitro groups it probably derives from the degraded hardwood lignin.

The remaining component which accounted for only 10% of the acid

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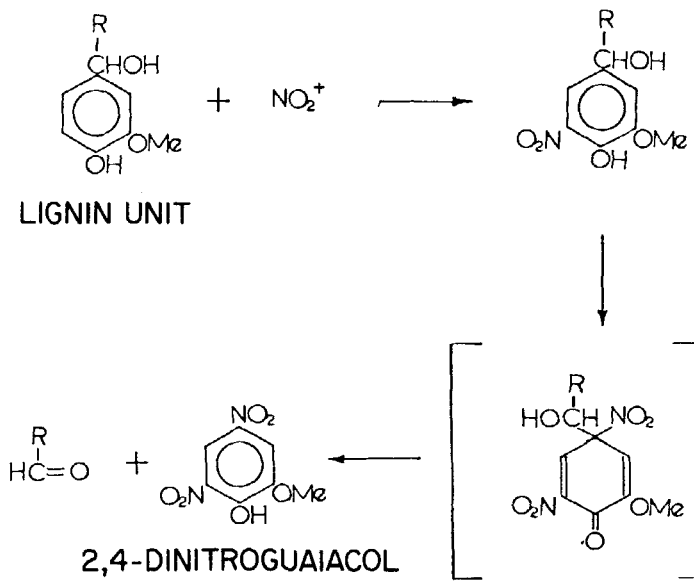
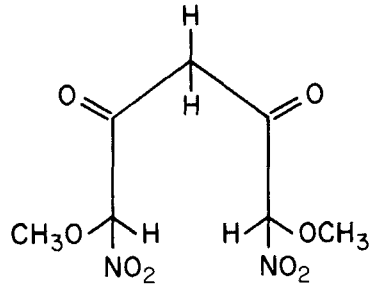


FIGURE 9 Mechanism for formation of 2-4-dinitroguaiacol from lignin.



NITRIC ACID DEGRADATION PRODUCT FROM MAPLE

FIGURE 10 Probable structure of the secondary component of the acid fraction from nitric acid treatment of sugar maple.

fraction is apparently either accumulated impurities from the large quantities of solvents used for isolation or other minor degradation products. The phenolic and neutral fractions have not been characterized at the time of writing. These two fractions represent a smaller percentage (0.09%) of the treated wood and therefore are probably of less significance to the chemical bonding mechanism than the acid fraction.

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CONCLUSIONS

1. *Oxidation* of the wood surface to primarily carboxyl groups is an important aspect of wood activation for surface bonding.
2. *Nitration* of the wood is an integral part of the activation process (with nitric acid) and nitro compounds may be important to wood bonding.
3. Both *hydrolysis* of wood polymers and *condensation* of lignin probably occur with nitric acid treatment.
4. Nitric acid activation appears to occur in two stages:
   Stage I—Lignin is primarily oxidized, nitrated, hydrolyzed and condensed at room temperature and xylan is extensively hydrolyzed.
   Stage II—The polysaccharides are further oxidized and hydrolyzed and some additional modification of lignin takes place at the higher temperature. The hardwood hemicellulose, xylan, appears to be the most severely altered through oxidation and hydrolysis.

This investigation has yielded information which promotes the understanding of the mechanisms of this unique wood bonding system. The picture is, however, by no means complete. It is hoped that the findings reported here, will aid future researchers in their attempts to characterize and commercialize the process of wood bonding by surface reactions.

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34. The assistance of Dr. John Ralph with the analysis of the wood degradation products is gratefully acknowledged.

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