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WOOD COLOR CHANGES BY AMMONIA FUMING

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This paper studies the influence of ammonia gas on wood color changes in response to an increasing demand for dark colored wood specimens. The darker wood color in ammonia fuming is accomplished through chemical reactions between ammonia gas and wood compounds. We exposed oak, maple, spruce, and larch wood samples to ammonia gas for 16 days. During fuming, the color changes were studied using CIE *L*a*b** parameters. After fuming, the changes in extractives content, tannin, and nitrogen content were analyzed. The chemical changes of wood and residues of wood extractives after fuming were analyzed by FTIR spectroscopy. Oak wood reacted intensively with ammonia gas in a very short time, and the darkening was prominent for all the investigated wood species. It was established that tannin had no major influence on color changes of maple and larch wood in the ammonia-fuming process. The FTIR spectra of fumed wood indicated involvement of carbonyl groups, and the FTIR spectra of wood extractives indicated involvement of carbonyl, aromatic, and alcohol groups in reaction with ammonia gas.

INTRODUCTION

The color of wood is an appearance-related attribute that could have a significant influence on consumer choice for wood furniture and floors. The color of wood can be altered to meet consumer preferences. One of the methods of altering wood color is fuming. Fuming is the traditional method for coloring wood and is accomplished through chemical reactions between ammonia gas and wood compounds. Fuming tends to color wood uniformly, giving it a natural look. Depending on the duration of fuming and the wood properties, the color can range from light brown to chocolate brown or black. The ammonia-fuming method became popular with many of the furniture makers and manufacturers during the Arts and Crafts movement in the early 1900s (Rodel 1999). Fuming created the classic rich warm brown color and accentuated the ray fleck that is most notable in quarter-sawn white oak (Peipher 2010).

The process of fuming has recently gained popularity due to the increasing demand for dark-colored wood species. Unlike traditional surface ammonia fuming used by furniture makers, the modern industrial fuming technique utilizes environmentally-friendly vacuum-pressure technology. This advanced process allows for good wood fiber saturation, yielding greater color intensity over the entire depth of the wood. With proper treatment, light-colored wood is darkened and may imitate exclusive timber. For this reason, it is frequently applied in furniture and flooring (Weigl *et al.* 2012).

There are a limited number of studies on changing wood color by ammonia fuming. The color reaction of ammonia-fumed oak wood was found to be possible only in combination with the availability of atmospheric oxygen (Tinkler 1921). Weigl *et al.* (2009a) investigated the effect of fuming on color change of 38 wood species. They reported the highest color change for black locust (*Robinia pseudoacacia* L.) and the lowest for black walnut (*Juglans nigra* L.). Miklečić *et al.* (2012) established that ammonia-fumed oak wood had better color resistance against UV radiation than heat-treated oak wood. Weigl *et al.* (2007) showed that ammonia fuming could be an effective way of pre-aging wood, resulting in stabilized color for some species. Color change of wood by ammonia fuming is based on changes in the chemical composition of wood (Weigl *et al.* 2009b). Partial inclusion of nitrogen, oxidation reactions, and the presence of tanning agents seem to be mainly responsible for color changes due to ammonia treatment (Weigl *et al.* 2009a). Pawlak and Pawlak (1997) reported that three types of chemical reactions are likely to occur between liquid ammonia and wood: 1.) Ammonia reacts with carboxylate groups and forms ammonium salts; 2.) Ammonia reacts with aldehyde and ketonic groups, producing imines; 3.) Ester functional groups react with the formation of amides. However, there is a lack of information concerning chemical changes in fumed wood.

The aim of this work was to establish the influence of wood species, extractives content, and length of exposure to ammonia gas on color change of wood during ammonia fuming. FTIR spectroscopy was used for analyzing the chemical changes in wood and wood extractives.

EXPERIMENTAL

Wood Samples
Radial-textured heartwood samples of oak (*Quercus robur* L.), maple (*Acer pseudoplatanus* L.), spruce (*Picea abies* L.), and larch (*Larix decidua* Mill.) wood were used in this study. Sample dimensions were 74 mm x 2.5 mm x 300 mm (R x T x L), and they had no visible defects. All wood samples were conditioned to 8.4% moisture content at $23 \pm 2°C$ and $50 \pm 5\%$ relative humidity.

Ammonia Fuming
Twelve samples of each wood species were fumed with ammonia, and one sample was kept as an untreated reference. Fuming was performed in closed plastic chambers in the presence of air at $23 \pm 2°C$ and $50 \pm 5\%$ relative humidity. Air volume within the chamber was 0.0135 m³. Samples were set around a petri dish containing 40 mL ammonium hydroxide (concentration 25 %) for 1, 2, 4, 7, 11, and 16 days. After each period of exposure to ammonia gas, two samples were withdrawn and ventilated until the ammonia odor vanished.

Prior to measurements, the samples were conditioned for two months at $23 \pm 2°C$ and $50 \pm 5\%$ relative humidity.

Color Measurements

Color measurements were performed before and after fumigation with a portable spectrophotometer Microflash 100d produced by Datacolor (d/8° measuring geometry, 10° standard observer, D65 standard illuminate). Measurements were taken on the same 24 locations on the sample, and the arithmetic mean of 48 measurements was calculated for each wood species. The overall color change ΔE^* was measured using the CIE $L^*a^*b^*$ color measuring system, where L^* describes the lightness, and a^* and b^* describe the chromatic coordinates on the green-red and blue-yellow axes, respectively. ΔE^* was calculated as follows,

$$\Delta E^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2} \qquad (1)$$

where ΔL^*, Δa^*, and Δb^* are the differences between the initial and the final values (before and after fuming) of L^*, a^*, and b^*, respectively.

Extractives Content

Extractives content was determined in wood samples before and after 16 days of ammonia fuming, using an appropriate solvent in a Soxhlet apparatus (TAPPI T204cm-97). For each wood species, 3 g of a ground and sieved (30-mesh size) sample was extracted with distilled water (hot water extractives – HWE) which is polar solvent and a 1:1 v/v% ethanol/benzene mixture (ethanol-benzene extractives – EBE) which is polar-nonpolar solvent through 16 h, at 150°C. Extractives content was determined after isolation and drying to constant mass using the gravimetric method. The three parallel measurements were performed.

Tannin Content

Tannin content was determined in three samples of each wood species before and after 16 days of fuming. Two grams of the ground and sieved (passed through 50-mesh screen) sample was boiled for four hours in 100 mL of water and filtered. The tannin content was determined using the Löwenthal method by adding 1 mL of sample and 5 mL of indigo carmine to a 300 mL Erlenmeyer flask and adding 200 mL distilled water. This solution was titrated against the potassium permanganate solution (N/40 or 0.005M) until the royal blue faded to a light green. The solution was then titrated drop-wise until the lime green changed to yellow; this value was recorded as X mL. A blank titration was carried out using 5 mL of indigo carmine alone in 200 mL distilled water; this value was recorded as Y mL (Tinkler 1921). The total tannin content was calculated using the following equation:

$$\text{Total Tannin (\%)} = (X/Y)/10 \qquad (2)$$

Nitrogen Content

Nitrogen content was determined before and after 16 days of ammonia fuming. The wood sample was ground and sieved (50-mesh size), and 200 mg of the oven-dried sample was analyzed. Total nitrogen content in the samples was determined using the dry combustion method with a Vario Macro CHNS analyzer. The nitrogen content of the

sample was determined by heating the sample in an oxidation column to a temperature of at least 900°C in the presence of oxygen gas (the temperature of the oxidation column was 1150°C, $p(O_2)$ = 2.5 bar, and $V(O_2)$ = 10 to 75 mL) and in the presence of WO_3 as a catalyst for complete combustion of the sample (Zgorelec 2009). The three parallel measurements were performed.

FTIR Spectroscopic Analysis

Chemical changes in unfumed and ammonia-fumed wood samples were analyzed with a Perkin Elmer Spectrum One spectrometer equipped with an ATR unit and chemical changes of extractives soluble in hot-water (HWE). Extractives soluble in ethanol-benzene were analyzed on a Shimadzu 8400S spectrometer using the KBr pellet method at a resolution of 4 cm^{-1} ranging from 400 to 4000 cm^{-1}. Standard Ø13 mm diameter pellets were prepared by mixing and pressing 10 mg of the dried wood extractive sample in 300 mg of KBr for 5 min under 200 bar pressure. The three parallel measurements were performed. The obtained FTIR spectra were further processed using the computer software, Spectrum One (ver. 5.0.1).

RESULTS AND DISCUSSION

Color Changes

Table 1 shows the L^*, a^*, and b^* values before and after 16 days of ammonia fuming for all studied wood species. After 16 days of ammonia fuming, the parameter L^* changed the most. The a^* value of oak wood decreased slightly after 16 days of ammonia fuming, while for other studied species, the a^* value increased after fuming. The b^* value decreased for oak and larch wood and increased for maple and spruce wood compared to unfumed samples.

Table 1. L^*, a^*, b^* Values Before and After 16 days of Ammonia Fuming

Wood species	Unfumed samples			Fumed samples		
	L^*	a^*	b^*	L^*	a^*	b^*
Oak	60.9 (2.48)[a]	7.5 (0.33)	23.0 (0.71)	35.5 (2.09)	6.7 (0.20)	14.4 (1.32)
Maple	83.3 (2.04)	4.4 (0.73)	20.8 (0.58)	54.2 (2.05)	10.0 (0.28)	25.8 (0.62)
Spruce	83.2 (0.53)	3.8 (0.19)	25.9 (1.02)	70.0 (0.58)	6.6 (0.37)	30.0 (0.67)
Larch	66.7 (0.60)	12.2 (0.47)	29.1 (0.66)	39.9 (1.22)	12.2 (0.64)	22.4 (0.99)
[a] The values in parentheses are standard deviations						

Color changes (ΔE^*) of oak, maple, spruce, and larch wood during ammonia fuming are presented in Fig. 1a. Oak and maple wood (representatives of hardwoods) exhibited greater color change during ammonia fuming compared to spruce and larch wood (representatives of softwoods). This result is also obtained by Weigl *et al.* (2009a). Compared to oak wood, the other investigated wood species exhibited more pronounced color changes after 16 days of fuming than after one day of fuming. This indicates that oak wood reacted intensively with ammonia in a very short time, while the reaction of ammonia with maple, larch, and spruce wood occurred more slowly.

The results of changes in $\Delta L*$ for oak, maple, spruce, and larch wood during ammonia fuming are presented in Fig. 1b. Trends in the change of lightness in studied wood samples were similar to overall color changes but with different direction, and all studied wood samples darkened during fumigation. The change in $\Delta L*$ had the highest contribution to the overall color changes ($\Delta E*$) after ammonia fuming, compared to $\Delta a*$ and $\Delta b*$ (Fig. 1).

The changes in color coordinate $\Delta a*$ during fuming were smaller than changes in color coordinate $\Delta b*$. Figure 1c shows that larch wood exhibited very small changes in $\Delta a*$ value. The $\Delta a*$ values for maple and spruce wood were positive during fuming, indicating an increase of red hue. Oak wood had negative values of $\Delta a*$ during fuming, indicating a decrease of red hue. The color coordinate $\Delta b*$ changed more in oak and larch wood subjected to ammonia fuming than in maple and spruce wood (Fig. 1d). Ammonia fuming of maple and spruce wood generally resulted in an increase of yellow hue; ammonia fuming of larch resulted in a decrease of yellow hue. The color coordinate $\Delta b*$ of oak wood at the beginning of fuming was greatly reduced, after which it became constant and then increased after 11 days. Color coordinate $\Delta b*$ for oak wood had a large contribution to the overall color changes ($\Delta E*$) during ammonia fuming, and for larch wood the color coordinate $\Delta b*$ contributed to the overall color changes ($\Delta E*$) only in long term treatment.
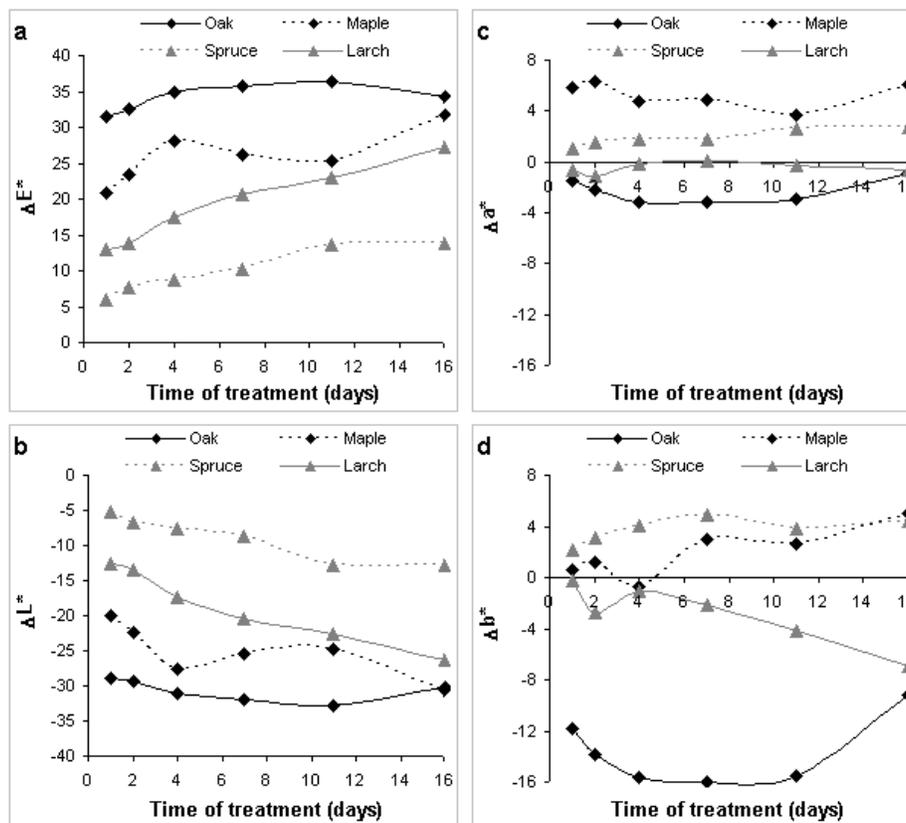

Fig. 1. Change in color during ammonia fuming: a) Δ*E**, b) Δ*L**, c) Δ*a**, d) Δ*b**

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Extractives, Tannin, and Nitrogen Content Analysis

The most important substances extractable by hot water are condensed tannins and water-soluble low-molecular weight carbohydrates (Nzokou and Kamdem 2006). The substances extractable by an ethanol-benzene mixture include aromatic compounds of intermediate polarity and some small amounts of non-polar molecular weight aliphatics (Ajoung and Breese 1998). The results of extractives content in oak, maple, spruce, and larch wood before and after 16 days of ammonia fuming are presented in Table 2. The table shows that the content of extractives soluble in hot water (HWE) and extractives soluble in ethanol-benzene (EBE) was reduced after 16 days of ammonia fuming in all studied wood samples except in larch wood, in which the HWE content increased compared to extractives content in unfumed wood. In fumed oak wood, there was a greater reduction in HWE content compared to EBE content (HWE by 13.1% and EBE by 8.4%). In contrast, fumed maple and spruce wood showed a greater reduction in EBE than HWE content compared to extractives content in unfumed wood (maple: HWE by 5.7% and EBE by 41.2%; spruce: HWE by 13.2% and EBE by 46.8%). In fumed larch wood, EBE was reduced by 55.7% and HWE content was increased by 3.3%. The reduction in extractives content after ammonia fuming could be due to the reaction of ammonia with extractives and the formation of less soluble compounds. The increase in HWE of larch wood is probably due to the reaction of ammonia with wood compounds, forming small, polar organic compounds soluble in water. The changes in extractives content after fuming suggest that ammonia reacts more strongly with EBE in maple, spruce, and larch wood than with HWE. In contrast, in oak wood, ammonia reacted more strongly with HWE, which could be related to the tannin content. The very high content of HWE for larch wood before fuming could be due to the content of arabinogalactan, polyose soluble in hot water (Gierlinger *et al.* 2004).

Extractives residues removed by hot water and the ethanol-benzene mixture were brown, but HWE were darker in color than EBE. This could be due to the higher tannin content in HWE. After fuming, all extractives darkened, especially HWE of oak wood, which became black, indicating a possible reaction of ammonia with extractives.

Table 2. Extractives Content in Wood Before and After 16 days of Ammonia Fuming

Wood species	Unfumed samples		Fumed samples	
	Extractives soluble in hot water (%)	Extractives soluble in ethanol-benzene (%)	Extractives soluble in hot water (%)	Extractives soluble in ethanol-benzene (%)
Oak	12.72	1.90	11.06	1.74
Maple	5.47	2.43	5.16	1.43
Spruce	5.38	3.55	4.67	1.89
Larch	25.97	3.41	26.83	1.51

Table 3 shows the results of measured nitrogen and tannin content in oak, maple, spruce, and larch wood before and after 16 days of ammonia fuming. The highest tannin content before fuming was determined in oak wood, and that content was the most reduced after fuming (3 times), which suggests that the ammonia reacted with tannin.

This could be the reason for reduction of HWE in oak wood and for the highest color changes of oak wood after fuming. Results in Table 3 also suggest that there was no change in tannin content of larch and maple wood before and after fuming. The tannin content in spruce wood before fuming is higher than in maple and larch wood, but the color change after fuming in spruce wood was lower than in maple and larch wood. This indicates that tannin has no major influence on color changes of maple and larch wood in the ammonia-fuming process.

Table 3. Nitrogen and Tannin Content in Wood Before and After 16 Days of Ammonia Fuming

Wood species	Tannin in unfumed samples (%)	Tannin in fumed samples (%)	N in unfumed samples (%)	N in fumed samples (%)
Oak	15	5	0.107	1.815
Maple	2.5	2.5	0.034	0.586
Spruce	4	2	0.034	0.499
Larch	2	2	0.011	0.576

In Table 3 it can be observed that oak wood had the highest nitrogen content after fuming, followed by maple and larch wood, and spruce wood had the lowest nitrogen content after fuming. This pattern is associated with the intensity of wood color changes after fuming, which is in agreement with the research of Petric *et al.* (2004). The increase in nitrogen content indicated that the chemical reaction occurred between structural wood components and ammonia.

We have tried to find correlations between color changes (ΔE^*) and nitrogen, tannin, and extractives content in wood before fuming for all investigated wood species (Table 4). It can be seen that there is a significant correlation only between color changes and content of extractives soluble in ethanol-benzene (EBE). This indicates that the lower content of EBE in wood before fuming means the higher color changes after fuming.

Table 4. Pearson Correlation Coefficient Between Color Changes (ΔE^*) and Nitrogen, Tannin, and Extractives Content in Wood Before Fuming

Variable	Nitrogen content	Tannin content	HWE content	EBE content
ΔE^*	0.32	0.34	0.25	-0.77*
* Correlation is significant at the 0.05 level				

FTIR Analysis

After 16 days of wood fuming, the most pronounced changes in the FTIR spectra were observed in the region of 2000 to 400 cm^{-1} (Fig. 2). The most pronounced changes in the FTIR spectra after ammonia fuming were seen in oak wood (Fig. 2a), and this is in correlation with the highest color changes for oak wood after fuming (Fig. 1a). In the FTIR spectra of fumed oak, maple, and spruce wood, the band at 1734 cm^{-1} was strongly reduced (Fig. 2a, b, c). The band at 1734 cm^{-1} was assigned to the ester carbonyl peak (Pawlak and Pawlak 1997; Rosca *et al.* 2002; Ajoung and Redington 2004). The band

reduction at 1734 cm^{-1} and the formation of a new absorption shoulder at 1650 cm^{-1} in the FTIR spectra of fumed oak and maple wood can be explained by the reaction of ammonia with ester carboxyl groups and the formation of amides (Pawlak and Pawlak 1997). The peak reduction at 1734 cm^{-1} in the FTIR spectra of fumed spruce wood could be due to the reaction between ammonia and hemicellulose, presumably xylanes (Petric *et al.* 2004).
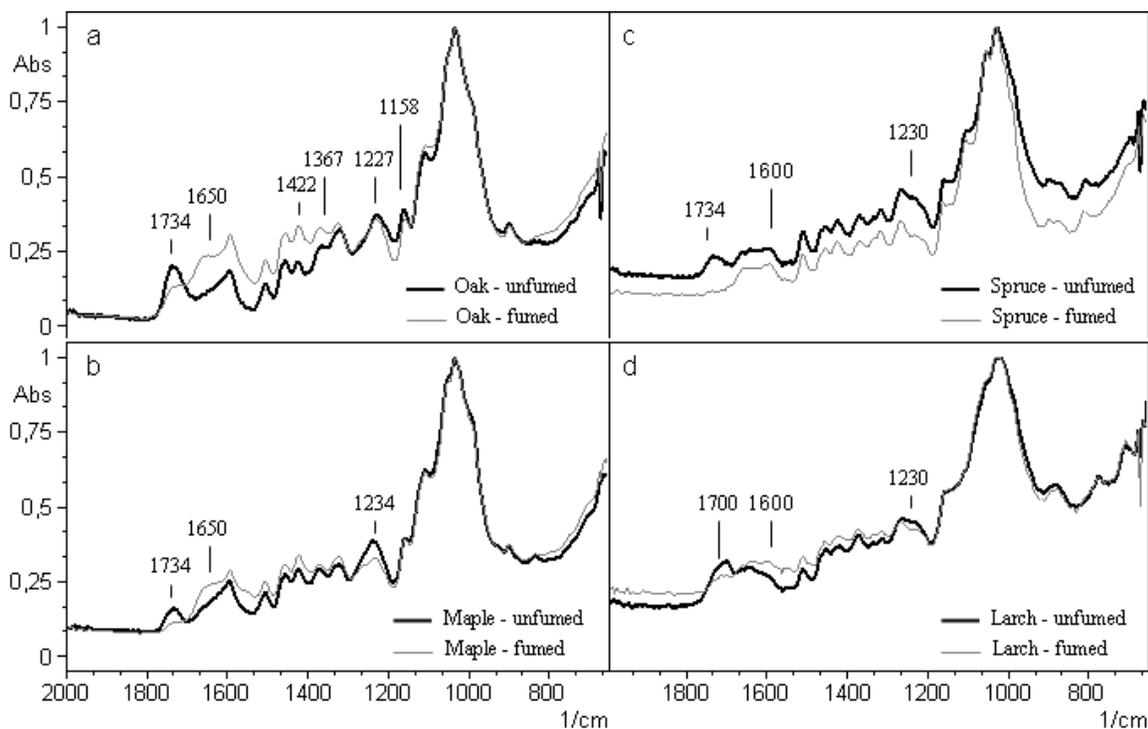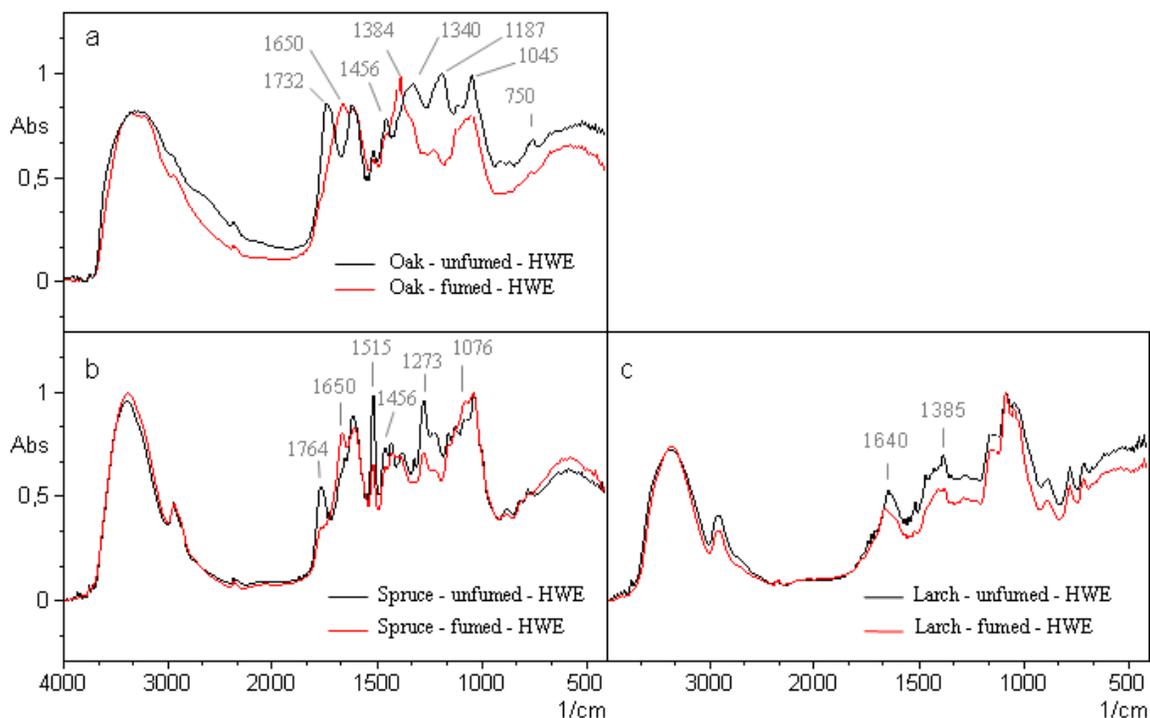

Fig. 2. FTIR spectra of oak, maple, spruce, and larch wood before and after 16 days of ammonia fuming

The band at 1700 cm^{-1} was reduced for ammonia-fumed larch wood, which can be due to the reaction of ammonia with carboxylic acid in the hemicellulose (Fig. 2d). The region around 1600 cm^{-1} in the spectra of all fumed wood samples still shows the absorption, but it has a different shape and relative intensity than in the unfumed wood. This suggests that ammonia salts are most likely formed in the hemicellulose or possibly lignin (Owen and Pawlak 1989). The reductions of bands at about 1230 cm^{-1} in maple, spruce, and larch wood could be due to the reaction of ammonia with xylanes. The increase of bands absorption at 1422, 1367, 1227, and 1158 cm^{-1} in oak wood are probably also caused by the formation of the ammonia salts (Fig. 2a). A great number of chemical reactions between wood and ammonia are possible. They could include the formation of quinoidal structures by oxidation of hydroquinones or phenols, the condensation of aldehydic functions in sugars with nitrogenous bases, condensation of α, and/or β-unsaturated aldehydes with reactive positions to form longer sequences of conjugated unsaturated linkages (Schuerch and Davidson 1971).

The changes in absorption bands of extractives could not be completely detected in the FTIR spectra of wood because some of the absorption bands of extractive

overlapped with bands of other wood compounds and because of the low content of extractives. Therefore, in this research we have also analyzed the FTIR spectra of extractives. Figures 3 and 4 show the FTIR spectra of isolated extractives for unfumed and ammonia-fumed wood. The FTIR spectra of HWE for maple wood are not presented because the hot-water extractives fractions became sticky when dried, and the pellets for FTIR measurement could not be made.

The FTIR spectra of fumed oak and spruce wood extractives that are soluble in hot water (HWE) showed a reduction of bands arising from the carbonyl groups (1732 and 1764 cm^{-1}), the aromatic groups (1456, 1515, 1340, and 750 cm^{-1}), and the alcohol groups (1187 and 1273 cm^{-1}) (Reusch 1999). This spectra also showed an increase of bonds arising from the amine groups (1650, 1046, and 1076 cm^{-1}) and the alkane groups (1384 cm^{-1}) (Fig. 3a, b). The change of absorption band at 1732 cm^{-1} in the FTIR of HWE for oak wood and the absorption band at 1764 cm^{-1} in FTIR of HWE of spruce wood could be due to the reaction of tannic acid with ammonia. Differences between the FTIR spectra of HWE of unfumed and fumed larch wood were very small, which could be expected because the change of HWE content in larch wood after fuming was very small; it can be only seen changing the shape of the peak at 1640 cm^{-1} and 1385 cm^{-1} (Fig. 3c). The peak at 1640 cm^{-1} was assigned to ketone bonding in taxifolin (Ruddick and Xie 1994), and a change in the shape of this peak could be due to the reaction of ammonia with taxifolin and the formation of amine groups.

Fig. 3. FTIR spectra of extractives soluble in hot water (HWE) of oak (a), spruce (b), and larch (c) wood before and after ammonia fuming

The FTIR spectra of fumed oak, spruce, and larch wood extractives soluble in ethanol-benzene (EBE) showed the reduction of bands arising from the carbonyl groups

(oak: 1717 cm^{-1}; spruce: 1734 cm^{-1}; and larch 1732 cm^{-1}), and an increase of bands arising from the amine groups (oak: 898 cm^{-1}; spruce: 1598, and 1212 cm^{-1}; larch: 1639, 1090, and 1030 cm^{-1}) (Fig. 4). Moreover, the FTIR spectra of EBE of fumed wood showed the reduction of bands arising from the aromatic groups (oak: 1600, 1456, and 1337 cm^{-1}; maple: 804 cm^{-1}; larch: 1455, 1380, and 800 cm^{-1}), and the reduction of bands arising from the alcohol groups (oak: 1220 cm^{-1}; maple: 1265 cm^{-1}; larch: 1262 cm^{-1}). A reduction of the carboxylic acids peak around 2925 cm^{-1} occurred in maple, spruce, and larch wood extractives soluble in ethanol-benzene (EBE).
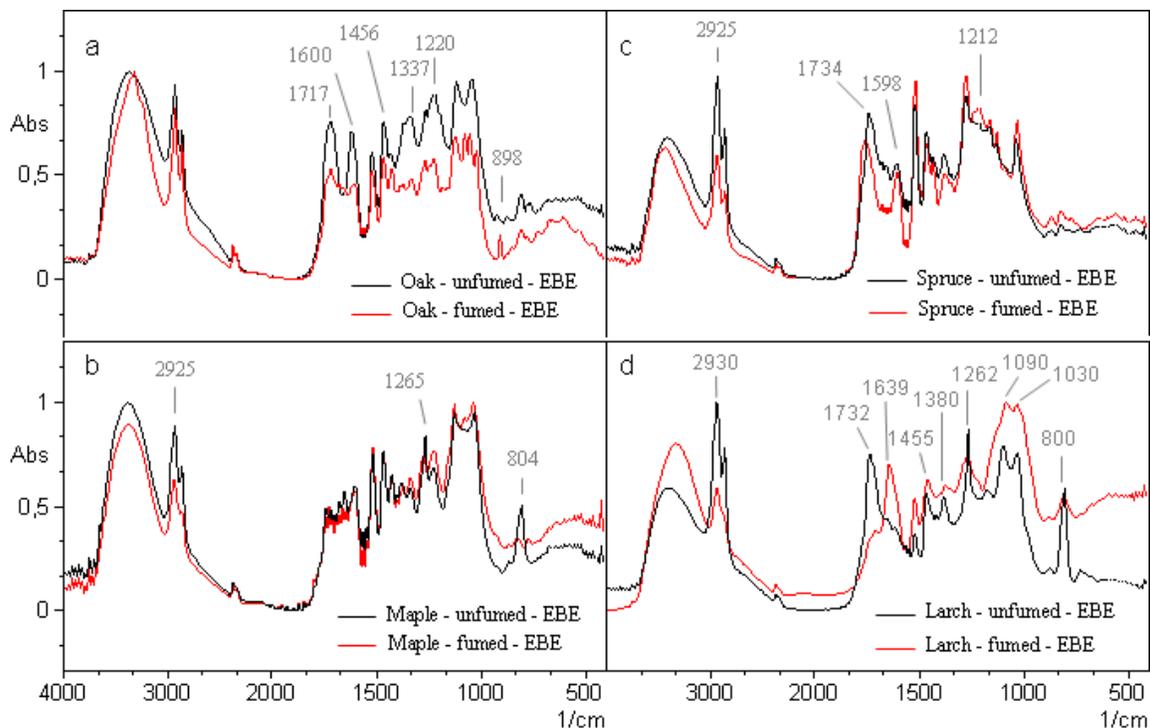
Fig. 4. FTIR spectra of extractives soluble in ethanol-benzene (EBE) of oak (a), maple (b), spruce (c), and larch (d) wood before and after ammonia fuming

From the FTIR data of extractives, it is very difficult to draw any firm structural conclusions, other than to deduce the presence or absence of certain functional groups because it is highly unlikely that the extract materials represent a single pure substance (Pawlak and Pawlak 1997). The chemical composition of wood extractives is very complicated since several hundreds have been identified in many different wood species (Horvath 2006).

The obtained FTIR spectra of extractives are different according to the wood species, the type of solvent, which could be expected due to the different content, and the type of extractives in studied wood species. A decrease of absorption bands of carbonyl, aromatic, and alcohol groups, and an increase of absorption bands arising from amine groups indicates possible chemical reactions of extractives with ammonia.

CONCLUSIONS

1. Oak wood reacted intensively with ammonia in a very short time, while the reaction of ammonia with maple, larch, and spruce wood occurred more slowly.

2. The decrement of L^* (darkening) was the most prominent for all investigated wood species.

3. Fuming resulted in greater changes in the content of oak wood extractives soluble in hot water, whereas fuming of maple, spruce, and larch wood resulted in greater changes in the content of extractives soluble in ethanol-benzene.

4. Fuming of oak wood resulted in the greatest reduction of tannin content. It was established that tannin had no major influence on color changes in maple and larch wood in the ammonia-fuming process.

5. Statistical significance was found only for color changes and content of extractives soluble in ethanol-benzene before fuming.

6. The reduction of carbonyl peaks in the FTIR spectra of fumed wood indicated the involvement of carbonyl groups of hemicelluloses in reaction with ammonia gas.

7. FTIR spectra of wood extractives indicated the involvement of carbonyl, aromatic, and alcohol groups in reactions with ammonia gas.

ACKNOWLEDGMENTS

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