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Wood Preservation by a Mixed Anhydride Treatment: A ¹³C-NMR Investigation of Simple Models of Polymeric Wood Constituents

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ABSTRACT: The treatment of wood by a mixed aceto/ oleic (or other fatty acid residue) anhydride promoted as a safe and environmentally friendly wood preservation system was examined quantitatively by liquid-phase ¹³C-NMR and solid-phase magic angle spinning DEC (proton decoupling) ¹³C-NMR through of all its different stages to determine which reactions occurred with simple model compounds of the polymeric constituents of wood. The preparation of the mixed aceto/oleic anhydride under different conditions was also undertaken. The anhydride formed, but its percentage yield was only 30%. The mix composed of unreacted acetic anhydride, the mixed aceto/oleic anhydride, and a large proportion of free acetic and oleic acid, which are used for wood preservation, yielded the acetylation of the lignin model compound (1) by the reaction of the acetic anhydride

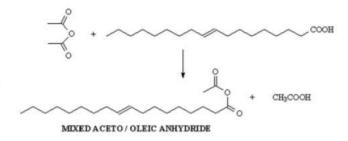
INTRODUCTION

The treatment of wood by acetic anhydride and other anhydrides by a nontraditional preservation method to improve its protection against biological attacks is well known.^{1–7} The industrial utilization and commercialization of wood treatment by acetic anhydride has started in a few countries. Interest in such treatments is increasing. There is no doubt, and many authors have shown it, that the acetic anhydride treatment considerably improves the durability and dimensional stability of timber.

Recently, a relatively novel approach was tried.⁸ Acetic anhydride was reacted with a fatty acid, such as oleic acid, up to a C24-length chain, to form a mixed acetic/fatty acid anhydride (e.g., aceto/oleic with it and (2) by the reaction of the acetic part of the mixed anhydride. In this reaction, all of the mixed anhydride was consumed. The oleic part of the mixed anhydride was unable to form esters with either lignin or wood holocellulose as it was far less reactive than the acetic part. Some acetylation of holocellulose occurred, and some traces of its oleic acid ester also occurred under some conditions. This system of treatment through a mixed anhydride appeared to consist of just an acetylation with acetic anhydride mixed with some oleic acid as a water repellent, both of which are already known processes. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 112: 44 51, 2009

Key words: additives; biomaterials; esterification; polysaccharides; stabilization

anhydride). This was in accordance with the follow-

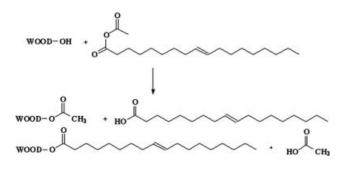


Previous research has demonstrated that the formation of mixed anhydrides is possible, albeit under certain conditions.⁹ The fixation of a fatty acid residue on reactive sites of holocellulose and lignin would occur by the treatment of wood with such a mixed aceto/oleic anhydride. This is in accordance with the following reactions:

1

ing reaction:

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Acetylation would then improve wood dimensional stability and durability.^{1–7} Furthermore, as fungal attack is at its most severe in moist conditions, the fixation of a fatty acid residue onto the wood by esterification would ensure its water repellence. This would yield greater protection of the timber against fungal attack. The fixation of oils in wood for this purpose has been demonstrated in previous research.^{10–13} This has been achieved either by high-temperature oil treatments^{14,15} or by ambient-temperature oil fixation by radical double bond opening and polymerization reactions.16,17 All of these systems have been used to fix the oil inside the wood, as loose oil would leak out. When the oil leaks out, the wood loses its water repellence and, hence, its resistance to fungal attack. Loose oil would also greatly interfere with water-based surface finishes, particularly when a wood finish is needed.

Thus, the study a different oil-fixation process⁸ held some interest for us. Previous research had not checked esterification by the oleic acid residue *in situ* in the wood. Esterification was only deduced by the extraction and recovery of acetic and oleic acid after the acid/alkaline hydrolysis of the treated wood.⁸ As unlinked oleic acid would be extracted too, there was no proof that the acids had formed the ester in the wood. Although esterification may occur when a pure mixed anhydride is used to treat wood, this may not be the case when the treatment is carried out with the reaction mix as proposed in the patent in ref. 8.

Through the investigation of the new approach with laboratory wood treatment experiments,¹⁸ it was impossible to either fix or maximize the fixation of the oleic residue in wood. It is for this reason that this investigation was carried out, with model compounds, to define (1) whether the mixed aceto/oleic anhydride formed, (2) whether another type of anhydride could be used to prepare a mixed anhydride of a similar type, and (3) once the mixed anhydride formed, whether the treatment of the wood with the nonpurified mixture, as described in the patent in ref. 8, could fix an oleic residue on the wood constituents.

EXPERIMENTAL

Sample preparation

For the preparation of the mixed aceto/oleic anhydride, 1 mol of acetic anhydride was reacted with 1 mol of oleic acid under different conditions, namely, at 20°C for 1 h, 20°C for 1 h in the presence of H₂SO₄, 140°C for 30 min, 140°C for 30 min in the presence of pyridine traces, and 140°C for 30 min in the presence of H₂SO₄.

As simple model compounds for the lignin and cellulose reaction, guaiacol and glucose were reacted as follows (phases a and b):

Reactions of raw mixed anhydride with glucose or guaiacol

- (a) Acetic anhydride + Oleic acid (molar ratio = 1 : 1), 20°C, 1 h. (b) Reaction product of (a) + Glucose water solution (1 mol of the reaction product : 1 mol of glucose), 80–100°C, 30 min.
- 2. (a) Acetic anhydride + Oleic acid (molar ratio = 1 : 1), 20°C, 1 h. (b) Reaction product of (a) + Guaiacol (1 mol of the reaction product : 1 mol of guaiacol), 80–100°C, 30 min.
- 3. (a) Acetic anhydride + Oleic acid (molar ratio = 1 : 1), 140°C, 30 min, + Pyridine. (b) Reaction product of (a) + Glucose water solution (1 mol of the reaction product : 1 mol of glucose), 80–100°C, 30 min.
- 4. (a) Acetic anhydride + Oleic acid (molar ratio = 1 : 1), 140°C, 30 min, + Pyridine. (b) Reaction product of (a) + Guaiacol (1 mol of the reaction product : 1 mol of guaiacol), 80–100°C, 30 min.
- 5. (a) Acetic anhydride + Oleic acid (molar ratio = 1 : 1), 140°C, 30 min, + Pyridine. (b) Reaction product of (a) + Ethanol (1 mol of the reaction product : 1 mol of guaiacol), 80–100°C, 30 min.
- 6. (a) Acetic anhydride + Oleic acid (molar ratio = 1 : 1), 20°C, 1 h. (b) Reaction product of (a) + Solid glucose (1 mol of the reaction product : 1 mol of glucose), 80–100°C, 30 min.
- 7. (a) Acetic anhydride + Oleic acid (molar ratio = 1 : 1), 140°C, 30 min, + Pyridine. (b) Reaction product of (a) + Solid glucose (1 mol of the reaction product : 1 mol of glucose), 80–100°C, 30 min.

Transesterification

- 8. (a) Acetic anhydride + Glucose water solution (molar ratio = 1 : 1), 20°C, 1 h. (b) Reaction product of (a) + Ethyl oleate (1 mol of the reaction product : 1 mol of ethyl oleate), 80–100°C, 30 min.
- 9. (a) Acetic anhydride + Guaiacol (molar ratio = 1 : 1), 20°C, 1 h. (b) Reaction product of (a) +

Ethyl oleate (1 mol of the reaction product : 1 mol of ethyl oleate), 80–100°C, 30 min.

Other reactions

- Glucose water solution + Oleic acid (molar ratio = 1 : 1), 20°C, 1 h.
- Glucose water solution + Oleic acid (molar ratio = 1 : 1), 140°C, 30 min.
- 12. Solid glucose + Oleic acid (molar ratio = 1 : 1), 20° C, 1 h.
- 13. Solid glucose + Oleic acid (molar ratio = 1 : 1), 140° C, 30 min.
- Glucose water solution + Ethyl oleate (molar ratio = 1 : 1), 20°C, 1 h.
- Glucose water solution + Ethyl oleate (molar ratio = 1 : 1), 140°C, 30 min.
- 16. Solid glucose + Ethyl oleate (molar ratio = 1 : 1), 20°C, 1 h.
- 17. Solid glucose + Ethyl oleate (molar ratio = 1 : 1), 140°C, 30 min.

The samples were analyzed by liquid-phase ¹³C-NMR. The spectra were obtained on a Bruker MSL 400 Fourier transform NMR spectrometer (Bruker, Wissembourg, France). The chemical shifts were calculated relative to $(CH_3)_3Si(CH_2)_3SO_3Na$ dissolved in D₂O for NMR shift control. The spectra were done at 62.90 MHz for a number of transients of approximately 1000. All of the spectra were run with a relaxation delay of 5 s and chemical shifts were accurate to 1 ppm.

The samples were analyzed by solid-state magic angle spinning (MAS)-DEC (proton decoupling) ¹³C-NMR. With the DEC technique, the spectra are quantitative, contrary to what would be obtained by cross-polarization/MAS. Spectra were obtained on a Bruker MSL 300 Fourier transform NMR spectrometer at a frequency of 75.47 MHz and at sample spin of 4.0 kHz. The impulse duration at 90° was 4.2 ms, the contact time was 1 ms, the number of transients was about 1000, and the decoupling field was 59.5 kHz, d1 = 60 s. Chemical shifts were determined relative to tetramethylsilane used as a control. The spectra were accurate to 1 ppm. The spectra were run with the suppression of spinning sidebands. The results of the spectra of acetic anhydride and oleic acid were as follows: (1) acetic anhydride: 168.2 ppm (C=O), 20 ppm (=CH₃)¹⁹ and (2) oleic acid: 179.1 ppm (-COOH), 129 and 127.3 ppm (C=C), 23-34 ppm (-CH₂-), 13 ppm (-CH₃).

RESULTS AND DISCUSSION

Figure 1 shows the ¹³C-NMR spectrum of the product issued from the reaction of acetic anhydride with oleic acid reacted at 140°C (within the preferred temperatures reported⁸) for 30 min (cf. with the ¹³C-NMR spectral data for acetic anhydride and oleic acid in the Experimental section). This reaction was also done at ambient temperature, at 140°C, and for a longer time (1 h) with or without catalyst. The NMR spectra were

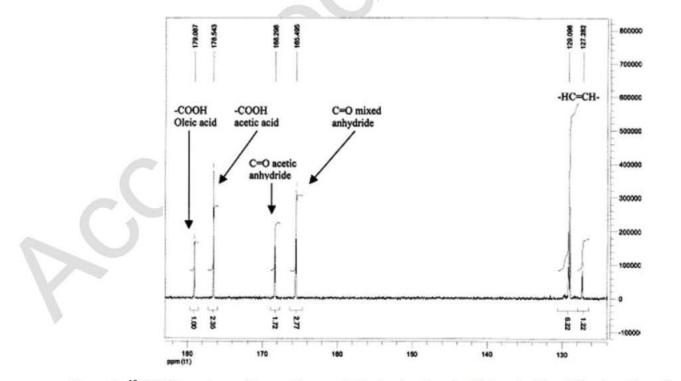


Figure 1 ¹³C-NMR spectrum of the reaction product mix of acetic anhydride and oleic acid (molar ratio = 1 : 1) reacted at 140°C for 30 min with a detail of the 124 183-ppm range.

in the Acetic Anhydride and Oleic Acid Reaction Product Mixes						
	140°C, H ₂ SO ₄ , 30 min	140°C, pyridine, 30 min	140°C, 30 min, no catalyst	20°C, 1 h, no catalyst		
Oleic acid Acetic acid Acetic anhydride Mixed aceto/ oleic anhydride	1.00 2.25 1.43 2.37	1.00 2.35 1.72 2.77	1.00 2.50 1.91 3.48	1.00 2.40 1.49 2.34		

TABLE I				
Integrals of the C=O of Acids and Anhydrides				
in the Acetic Anhydride and Oleic				
Acid Reaction Product Mixes				

done for all of these reaction products. Because no great differences were seen between the spectra of the products obtained under these different reaction conditions, only one spectrum (Fig. 1) is reported in detail here. Shown in Figure 1 are the bands of (1) the —COOH carboxyl groups of oleic acid (179.1 ppm) and acetic acid (176.5 ppm), (2) the \rangle C=O groups of acetic anhydride at 168.3 ppm (this signal varied between 168.2 and 170.2 ppm), and (3) a new band at 165.5 ppm, this being the >C=O on the oleate residue side of the mixed acetic/oleic anhydride. The C=C in oleic acid was observed at 129 and 127.3 ppm. The bands belonging to oleic acid different —CH₂—groups were seen between 20 and 34 ppm. The assignments are indicated in detail in Figure 3.

Two interesting conclusions can be drawn from these spectra: (1) the mixed anhydride did indeed form, and (2) considerable amounts of oleic acid not converted to the mixed anhydride, acetic anhydride left unreacted, or residual acetic acid were present in the mix at the end of the reaction. Thus, the percentage yield of the mixed anhydride was rather modest. As the NMR spectra were quantitative, the examination of the relative integrated areas of the different bands, presented in Table I and Table II, indicated that the yield of the mixed anhydride was relatively low, this being between 32 and 39% of the original reagents. The residual, unreacted acetic anhydride was 20-22%. This was to be expected, even at higher reaction temperatures, as the hydrolysis and reaction with water of acetic anhydride is relatively slow. This is so because only an interfacial reaction between the two unmixed liquids occurs.^{20,21}

It is the raw product mix that is used to treat timber according to what is defined in some of the patent claims. This is logical, as extraction and purification of the mixed anhydride from the reaction mix would be exceedingly costly. Thus, for the second part of the reaction, the raw product mix containing the mixed anhydride was reacted under a variety of conditions with glucose and guaiacol as simple model compounds of wood holocellulose and lignin. The reactions were carried out with both glucose dissolved at a high concentration in water and solid, undissolved glucose. The reactions with guaiacol were carried out with pure guaiacol. All of the reactions were carried out at 80–100°C. The more significant NMR spectra of the products of these reactions are shown in Figures 2–4 shift in Table III.

Shown in Figure 2 is the product mix of the reaction of the acetic anhydride and oleic acid with guaiacol at 80–100°C for 30 min. The bands that can be seen unaltered are the -COOH carboxyl groups of oleic acid (179.1 ppm) and acetic acid (176.5 ppm), the C=C of oleic acid at 129 and 127.3 ppm, and the oleic acid chain saturated carbons between 13 and 33 ppm. However, there were a number of new bands or bands in which the intensity varied. Thus, although the bands at 170.1 and 167.5 ppm belonged to the C=O of unreacted acetic anhydride, the band of C=O of the mixed anhydride that was at 165.5ppm in Figure 1 disappeared. This indicated that no mixed anhydride was left; it had all reacted. Furthermore, several new bands appeared. A band at 167.5 ppm was that of the C=O of an ester of guaiacol, with the shift clearly indicating the C=O of the acetate of guaiacol. The formation of the acetate of guaiacol was confirmed by the NMR spectrum shown in Figure 3, where only the acetate of guaiacol could form by the reaction of acetic anhydride and guaiacol. Here, too, the shift of the C=O was at 167.3 ppm. Supporting this were the four new bands between 139.2 and 150.5 ppm. The two smaller of these at 145.3-145.5 ppm belonged to the aromatic carbons linked to the phenolic -OH and -OCH3 groups of unreacted guaiacol.^{22,23} More interesting were the two new bands at 150.5 and 139.2 ppm. These belonged, respectively, to the aromatic C2 (150.5 ppm) linked to the methoxy group of an acetylated guaiacol and the aromatic C1 onto which acetylation occurred (139.2 ppm). The shifts of these bands further supported the finding that guaiacol acetylation occurred. The shifts of the different carbons belonging to unreacted guaiacol are indicated directly in Figure 2. To conclude, these model

TABLE II Compound Percentages in the Reaction Product Mixes in the Acetic Anhydride and Oleic Acid Reactions

	140°C, H ₂ SO ₄ , 30 min	140°C, pyridine, 30 min	140°C, 30 min, no catalyst	20°C, 1 h, no catalyst
Oleic acid Acetic acid	13% 30%	13% 30%	11% 28%	14% 33%
Acetic anhydride Mixed aceto/ oleic anhydride	22% 35%	22% 35%	21% 39%	21% 32%

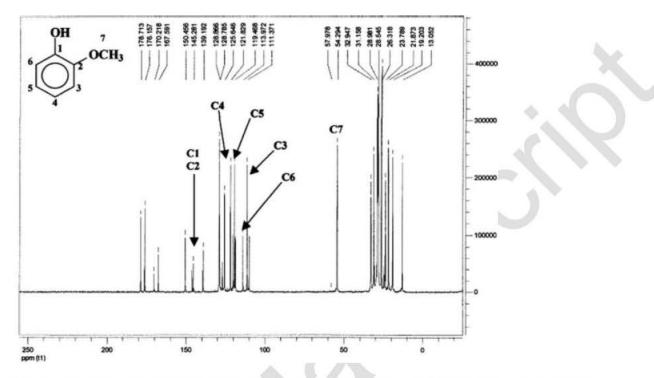


Figure 2 ¹³C-NMR spectrum of the reaction product mix of acetic anhydride and oleic acid (molar ratio = 1 : 1) reacted at 140°C for 30 min followed by its reaction at a molar ratio of 1 : 1 with guaiacol at 80 100°C for 30 min.

compound reactions indicated that the guaiacyl nuclei of lignin were esterified, which confirmed previous work directly on lignin,^{24,25} but appeared to exclusively form one ester, the acetate. The acetate was formed by the reactions of guaiacol with both the residual acetic anhydride and the mixed anhydride. The presence of only one ester indicates that all of the mixed anhydride reacted; hence, it was rather unstable and easily underwent reaction, with none of it remaining. However, this indicates that it was the acetate, the more reactive of the two residues, that alone reacted and esterified the model compound of lignin. Thus, the oleic acid, even if taking part with a poor yield in the formation of the mixed

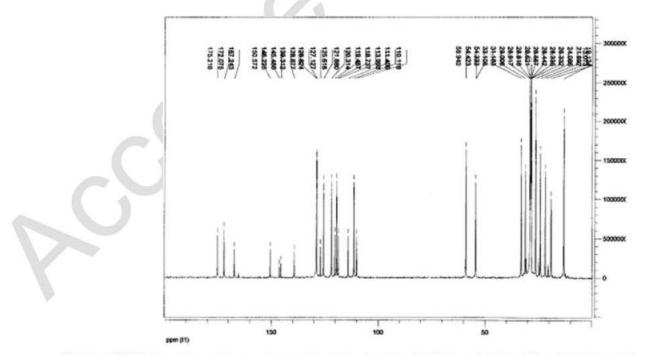


Figure 3: ¹³ NMR spectrum of the reaction product mix of acetic anhydride and oleic acid (molar ratio ¹/₄ 1 : 1) reacted Figure 3 C-at 20 C for 60 min with guaiacol followed by its reaction at a molar ratio of 1 : 1 with ethyl oleate at 80 100 C for 30 min.

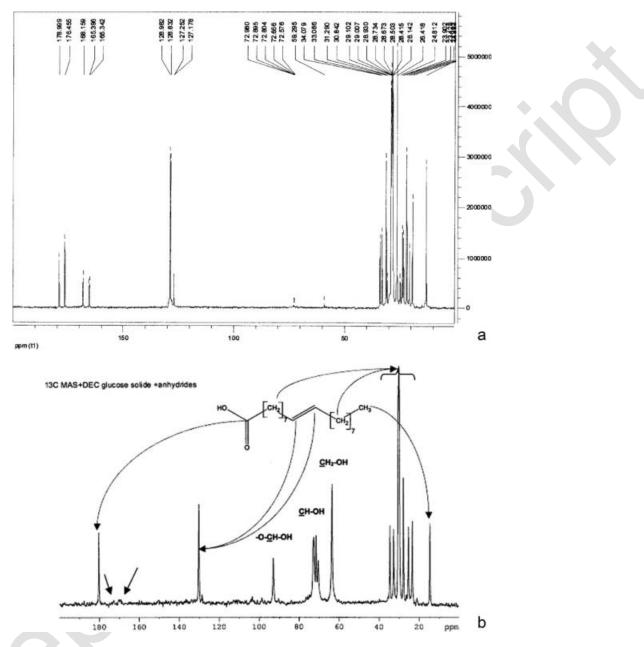


Figure 4 ¹³C-NMR spectra of the reaction product mix of acetic anhydride and oleic acid (molar ratio = 1 : 1) reacted at 20°C for 60 min followed by its reaction at a molar ratio of 1 : 1 with glucose at 80 100°C for 30 min. (a) Spectrum of the reaction with solid glucose. (b) MAS DEC ¹³C-NMR solid-phase quantitative spectrum of the filtered glucose solid at the end of the reaction with solid glucose in the absence of water.

anhydride, once the mix reacted with a simple lignin model, remained only in the form of unfixed, free oleic acid.

The NMR spectra of the prereaction of the acetic anhydride and oleic acid with a water solution of glucose, reported elsewhere,¹⁹ and with solid glucose were indicative.¹⁹ The NMR spectra¹⁹ of the two phases that formed in the reaction mixture, the water phase and the supernatant nonwater phase, showed that only very small traces of an ester formed, but this could equally be an acetate or an oleate, and small traces of oleic acid residue formed. Other than these traces, there was not any great amount of oleic acid or oleic acid residue or any anhydride. Almost all of this was contained in the supernatant fatty, water-immiscible layer, where only oleic acid and acetic acid were found to be present.¹⁹ This indicates that hardly any esterification (only traces) of the glucose hydroxyl groups occurred. The traces of ester observed belonged to an oleate, which indicates that little esterification of the wood constituents, such as cellulose and hemicelluloses, occurred. However, as the glucose was in water solution, this implies that acetylation occurred and that hydrolysis followed it.¹⁹ This was not the case for the oleate that, because of water repellence,

TABLE III
¹³ C-NMR Shift Assignments for the Acetic Anhydride
and Oleic Acid Reaction and the Reactions
That Followed It

Group	Shift (ppm)	
Oleic acid, COOH	178.7	179.1
Acetic acid, COOH	175.2	176.5
Glucose oleate ester, glucose acetate ester,		
and ethyl oleate, COO	172.0	172.9
Acetic anhydride, C O	168.2	170.2
Guaiacyl acetate ester, C O	167.2	167.5
Mixed aceto/oleic anhydride, C O	165.4	165.5
Guaiacyl acetate ester, aromatic		
C2 (OCH ₃)	150.5	
Unreacted guaiacol, aromatic C1 (OH)		
and C2 (OCH ₃)	145.3	145.5
Guaiacyl acetate ester, aromatic		
C1 (OOC)	139.2	
Oleic acid, HC CH	128.3	129.1 and
	127.1	127.3
Glucose, CH and CH ₂	59.9	95
Oleic acid, CH ₂	19.5	35
Oleic acid, CH ₃	13.0	13.2

could not form in any proportions other than traces because the bulk of the oleic residue was in a separate phase.

To avoid this problem, we repeated the reaction by reacting solid glucose with the acetic anhydride and oleic acid prereaction mix. The NMR spectra of the liquid phase are reported in Figure 4(a), where the presence of the two acids, acetic and oleic, are clearly visible along with the two anhydrides by the signals of their respective C=O's at 179, 176.5, 168.2, and 165.4 ppm. There was no glucose present as this was not soluble as there was no water. The quantitative solid-phase MAS-DEC 13C-NMR examination of the solid residues of the solid glucose after reaction in the heterogeneous phase is shown in Figure 4(b). Bands belonging to glucose and to some oleic acid were seen. There were only very small traces of the C=O groups of the two esters, namely, glucose acetate and glucose oleate (the very small bands at 171 and 173 ppm), which were almost drowned by the background noise. This result agrees with previous findings that the esterification of wood carbohydrates was always rather low and much lower than lignin.25

Shown in Figure 3 is the product of the reaction of the acetic anhydride and guaiacol prereaction (20° C, 1 h) mixed with ethyl oleate. This was done to see whether, after guaiacol acetylation, transesterification was possible and the oleic acid residue could be fixed as an ester. The spectrum showed the C=O of acetic acid (175.2 ppm), the C=O of the ethyl oleate (172.0 ppm) used, the C=O of the acetate of guaiacol (at 167.2 ppm), no acetic anhydride still unreacted, and the acetate of guaiacol peaks at 150

and 139 ppm. No transesterification appeared to occur, as the only oleate peak present was that of the ethyl oleate that was added to the mix.

The formation of the mixed anhydride according to the system envisaged by the patent in ref. 8 was attempted by the reaction under all of the same reaction conditions (either ambient temperature or 140°C and with or without catalyst) of oleic acid and maleic anhydride. No mixed anhydride was formed when the reaction was started with a cyclic anhydride such as maleic anhydride. The reaction product analyzed by quantitative MAS–DEC ¹³C-NMR (Fig. 5) showed that the two original reagents had not reacted and the mix consisted of free maleic anhydride and free oleic acid.

CONCLUSIONS

In conclusion, the reaction of acetic anhydride and oleic acid yielded a mixed aceto/oleic anhydride, but its yield was rather low at 30% to allow wood treatment without problems. The treatment of wood, as recommended in the relevant patent in ref. 8, did not yield the expected results.8 Thus, the raw mix composed of unreacted acetic anhydride, the mixed aceto/oleic anhydride, and a high proportion of free acetic acid and free oleic acid yielded the acetylation of wood lignin by (1) the reaction of the acetic anhydride with it and (2) the reaction of the acetic part of the mixed anhydride. In this reaction, all of the mixed anhydride was consumed, and none of it remained (which was not strictly the case with acetic anhydride). Thus, the conclusion is that such an anhydride is rather labile or unstable. The oleic part of the mixed anhydride apparently is not able to form esters on lignin because it is far less reactive than the acetic part. Carbohydrates are definitely much less readily esterified because they are polar enough

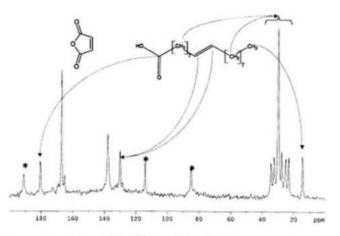


Figure 5 MAS DEC ¹³C-NMR solid-phase quantitative spectrum of the reaction product of oleic acid with maleic anhydride.

to repel the oleic residue. Some holocellulose acetylation occurs, and some traces, and no more than traces, of holocellulose oleic acid ester occur, too, under some conditions. Thus, the system of treatment promoted by the patent in ref. 8 of a mixed anhydride does work in a different way than that envisaged. There was no difference in production or the mixed anhydride, with the treatment system being just an acetylation with acetic anhydride mixed with some oleic acid or ester as a water repellant. Both are known processes. The same results can be achieved by the treatment of wood either with acetic anhydride followed by treatment with a water repellent or treatment with an unreacted mixture of acetic anhydride and a fatty acid. Thus, it cannot be considered a new process.

Such a process, however, causes considerable, additional problems in treated timber. First, the great amount of unfixed oleic acid is mobile and prone to eventually leak out of the timber, with a loss of water resistance and accompanying waste into the environment. Second, it is impossible to apply a water-based wood surface finish on a substrate loaded with a liquid, mobile fatty acid that repels them, a considerable problem today, when water-based finishes are favored for environmental reasons.

There are some solutions that can be suggested to solve the problems that have been outlined and that derive from the treatment system not doing what it had been thought to do.⁸ These are

- 1. To use an oil compatible surface finish, either based on a solvent compatible with the oil or soluble in the oil itself.
- 2. To wipe clean with an organic solvent the surface of the wood before it is applied to the finish for the finish to grip the wood. This could be, however, only a temporary measure because, as new, mobile oil comes to the surface, the finished film could well start to peel off much earlier than envisaged.
- 3. To react to an insoluble network of an saturated fatty acid by its reaction through the C=C bond, which would thus form a stable cross-linked network of polymerized unsaturated oil within the wood. These are systems that already exist and do work either by heat-induced crosslinking or by chemical-initiation-induced radical crosslinking reactions.^{14–17}

4. To graft the oil onto cellulose with the coordination complex between cerium IV and the hydroxyl groups of cellulose.²⁶

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