

# Self-Emulsifying Binders for Water-Borne Coatings— Synthesis and Characteristics of Maleated Alkyd Resins

Nina Heiskanen, Saila Jämsä, Leena Paaajanen, Salme Koskimies

VTT Technical Research Centre of Finland, FI-02044 VTT, Finland

Received 16 June 2009; accepted 14 March 2010

DOI 10.1002/app.32679

Published online 21 July 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Self-emulsifying binders have been prepared by reaction of long oil alkyd resins with maleated derivatives of fatty acids. These binders were dispersed in water without use of external surfactants and free from volatile organic compounds. The binders were evaluated based on their performance properties, including penetration and moisture repellency

ability against commercial references. According to this study, binders with interesting properties have been prepared. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 209–218, 2011

**Key words:** water-borne; coating; resins; modification; characteristics

## INTRODUCTION

Alkyd resins are widely used as binders in surface coatings due to their unique properties such as color and gloss retention, film flexibility and durability, and good adhesion.<sup>1,2</sup> In traditional alkyd paints, the alkyd is dissolved in organic solvent. Because of restrictive regulations, there is a need for paints with reduced volatile organic compounds.<sup>1–4</sup> Water-borne (WB) alkyd coatings are a practical solution combining the technical properties of alkyd resins with the environmental and health advantages of solvent-free coatings.<sup>1–4</sup>

WB alkyd resins have been known for decades, but the early materials had relatively poor performance.<sup>2–4</sup> These binders involved preparing a resin with a high-acid value, and thus, they suffered from limited hydrolytic stability and were typically too hydrophilic to be used in ambient temperature curable paints.<sup>5</sup>

Emulsions of alkyd resins are obtained by dispersing the alkyd into water. These WB binders need surface active agents to provide stability. After film formation, when water is evaporated, the paint still contains all the surfactants which are no longer needed for stabilization.<sup>3</sup> It is depicted that the conventional surfactants migrate to the film surface, and thus impair the film properties such as hardness and water resistance.<sup>6,7</sup> These problems may be avoided

by using reactive surfactants, which can be chemically incorporated into the polymer network during drying.<sup>1,6</sup>

Another way to overcome these problems is to use a binder polymer which is itself surface active, so that it can be emulsified with considerably less surfactant or no emulsifier at all.<sup>5,8</sup> These self-emulsifying resins can be achieved via introduction of stabilizing groups or segments into the polymer backbone or to the side chains.<sup>5,8</sup> For example, introduction of sufficient degree of pendant acid groups, followed by neutralization makes the resins water-dispersible. Moreover, high-acid values are not needed and the binder largely loses its hydrophilic properties upon drying.<sup>5</sup>

In this work, the focus was to prepare self-emulsifying, to air-drying alkyd binders, and to study their performance properties. The binders were prepared by reaction of long oil alkyd resins with maleated derivatives of fatty acids. These binders were dispersed in water without use of external surfactants and free from volatile organic compounds. The binders were evaluated based on their penetration and film formation ability, as well as water repellency and drying property.

## EXPERIMENTAL

### Materials

All the reagents and ingredients: trimethylolpropane (TMP; Perstorp, Perstorp, Sweden), pentaerythritol (PE; Perstorp, Perstorp, Sweden), isophthalic acid (IPA; Aldrich, Steinheim, Germany), benzoic acid (BzA, Aldrich, Steinheim, Germany), tall oil fatty acids (TOFA, Forchem, Rauma, Finland) and maleic

Correspondence to: N. Heiskanen (nina.s.heiskanen@gmail.com).

Contract grant sponsor: Finnish Funding Agency for Technology and Innovation (Tekes).

anhydride (MA, Sigma-Aldrich, Steinheim, Germany), potassium hydroxide (KOH) 45 wt % solution in water (aqueous KOH; Sigma-Aldrich, Steinheim, Germany), polyethylene glycol 300 (PEG 300; Fluka, Buchs, Switzerland), *ortho*-phosphoric acid ( $\text{H}_3\text{PO}_4$ ; Fluka, Buchs, Switzerland), and aqueous ammonia 25 wt % (Sigma-Aldrich, Steinheim, Germany) were used as received.

Commercial WB binders were used as reference. The references were: a WB binder for wood stains and priming based on long oil oxidatively drying alkyd, a WB binder recommends for use in exterior paints and wood stains based on long oil TOFA-based alkyd, and a WB vegetable oil based wood oil emulsion. For further reference in the text, the references will be designed as WB1, WB2, and WB3, respectively. A cobalt drier with a metal content of 8% was used, and the drier was added prior the film preparation as 0.1 wt % content of cobalt based on the binder solid content.

### Synthesis of conjugated fatty acids

Conjugated TOFA were prepared as reported previously.<sup>9,10</sup> That is, to a 1000 mL five-necked round-bottomed flask equipped with Dean-Stark apparatus, condenser, nitrogen inlet, thermometer, and mechanical stirrer was added PEG 300 (300 g), TOFA (295.5 g), and aqueous KOH (45 wt %, 135 mL). The resulting mixture was heated at 140°C for 3 h with vigorous stirring. During heating, boiling of water occurred and water was evaporated of the system. After cooling to below 100°C, the reaction mixture was acidified with  $\text{H}_3\text{PO}_4$  (85 wt %, 111 mL) and the mixture was heated for 0.5 h at 95°C. The upper fatty acid layer was separated and washed twice with  $\text{H}_3\text{PO}_4$  (60 wt %, 111 mL) at 95°C for 30 min to remove excess PEG and water. The conversion of linoleic acid to conjugated linoleic acid was confirmed by  $^1\text{H-NMR}$  spectroscopy.

### Synthesis of TOFA based alkyd resins

The alkyd was prepared according to nonsolvent procedure. That is, to a 1000 mL five-necked round-bottomed flask equipped with Dean-Stark apparatus, condenser, nitrogen inlet, thermometer, and mechanical stirrer was added TOFA (372.6 g), isophthalic acid (55.9 g), and pentaerythritol (71.5 g). All the ingredients were heated together at temperature of 230–260°C, under stirring and a stream of inert gas until the desired end-point was reached. The by-product water was removed by sparging inert gas continuously from bottom of the reactor carrying away water vapor from the reaction. The progress of the reaction was monitored by taking samples from which the acid value and viscosity were determined.

### Synthesis of conjugated TOFA based alkyd resins

The alkyd was prepared as reported previously.<sup>9</sup> That is, the mixture of TOFA (205.9 g), conjugated TOFA (52.85 g), isophthalic acid (74.8 g), benzoic acid (73.2 g), pentaerythritol (65.3 g), and trimethylolpropane (28.1 g) were heated at temperature of 220–240°C under stirring and a stream of inert gas until the desired end-point was reached.

### Synthesis of maleic anhydride modified TOFA

A typical procedure used for maleation of TOFA was as follows. TOFA (700 g) was weighted to a reaction flask. The flask was equipped with heating device, mechanical stirrer, condenser, and nitrogen inlet. The stirred solution was heated to 180°C and maleic anhydride (48.8 g) was added in portions during 2 h. After the addition, the reaction mixture was heated and stirred at 200°C for additional 2 h.

### Preparation of self-emulsifying maleated binders

Methods to prepare maleated alkyd resins and maleated alkyd hybrid resins have been published earlier.<sup>5,11–13</sup> In our work, different types of maleated derivatives and alkyd resins were used. Two types of alkyds were used differencing based on their oil length and also by ingredients used. One of the alkyds was TOFA-based, long oil alkyd (oil length of 85%). Another alkyd was composed both of TOFA and conjugated TOFA with an oil length of 60%. Maleation of TOFA was carried out separately. The binders were prepared by reaction of the alkyd resin and maleated TOFA, followed by maleic anhydride ring opening and neutralization. The binders were prepared following already known technique.<sup>11</sup> That is, mixture of maleated TOFA (50 g) and corresponding alkyd resin (100 g) was stirred and heated at 120°C for 3 h. Then, water (2.5 g) was added and heating was continued at 100°C for 2 h under stirring. Then the mixture was allowed to cool down and the pH of the binder was set to value of 7 with aqueous ammonia. Our procedure did not contain any organic co-solvents.

Emulsions with solid content of 45 wt % were prepared by adding water (550 g) dropwise into the binder (450 g) under heating and stirring at 50°C. After the water addition, two different methods were utilized: (1) the emulsion was further homogenized with high-shear homogenizer (Ultra-Turrax T25 basic, IKA-WERKE) or (2) the pH of the emulsion was further set to value of 8.8 and no high-shear homogenization was performed.

TABLE I  
Characteristics of the Alkyd Resins Synthesized

	Oil length (%)	AV (mg of KOH/g) <sup>a</sup>	OH (mg of KOH/g) <sup>b</sup>	Viscosity (P)
Alkyd 1	85	13	27	8.6 <sup>c</sup>
Alkyd 2	85	5	–	5.6 <sup>c</sup>
Alkyd 3	60	15	38	6.2 <sup>d</sup>
Alkyd 4	60	13	–	6.4 <sup>d</sup>

<sup>a</sup> Acid value.

<sup>b</sup> Hydroxyl value (5% OH-equivalent excess).

<sup>c</sup> Determined at the temperature of 50°C.

<sup>d</sup> Determined at the temperature of 75°C.

### Characterization

Viscosity was measured with an analogue, single speed motor, variable temperature control model (between 25°C and 150°C), cone and plate viscometer by Research Equipment London. The viscosity value was determined in Poises (viscosity range of 0–10). The viscosity value was measured at the temperature of 50°C when measurable. Temperature of 75°C was used with resins of higher viscosity.

The acid value (mg of KOH/g of sample) was determined with titrimetric method. A known amount of sample was dissolved in ethanol-toluene (1 : 1) solution and titrated with KOH solution using phenolphthalein as color indicator. The acid value was calculated according to the following equation:

$$\text{Acid value} = (A \times N \times 56.1) / W$$

Where  $A$  = consumption of KOH solution (mL),  $N$  = normality of the KOH solution, and  $W$  = weight of sample (g).

With some samples also hydroxyl value (mg of KOH/g of sample) was determined by determining the number of milligrams of KOH required to neutralize the amount of acetic acid bound in 1 g of fatty material after acetylation with acetic anhydride.

The pH values were measured by means of a digital pH meter (Orion Model SA 520 by Orion Research Incorporated Laboratory Products). The pH electrode was calibrated at 25°C with standard buffer solutions at pH 7.00 and 10.00.

NMR spectra were measured with Varian, Mercury-VX 300 MHz spectrometer, and the measurements were made at temperature of 23°C. The chemical shifts were referenced against the solvent: chloroform- $d_1$  ( $\text{CDCl}_3$ ) using  $\delta$  values of 7.27 ppm ( $^1\text{H}$ ) and 77.0 ppm ( $^{13}\text{C}$ ).

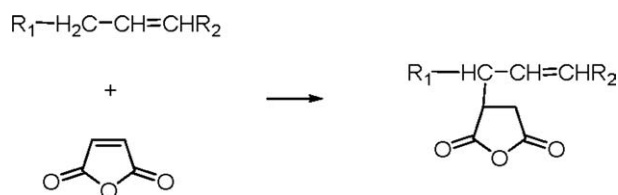
Gel permeation chromatography (GPC) was performed with a Waters Alliance 2690 instrument using Waters UV detector and 7.8 mm  $\times$  300 mm Styragel capillary columns with separative power between 100 and 500,000 g/mol. The calibration was performed with polystyrene standards with molecu-

lar weight between 468 and 177,000 g/mol. Tetrahydrofuran (THF) was used as eluent with a flow rate of 1.0 mL/min. Solutions of concentration  $\sim$  1 mg/mL were used.

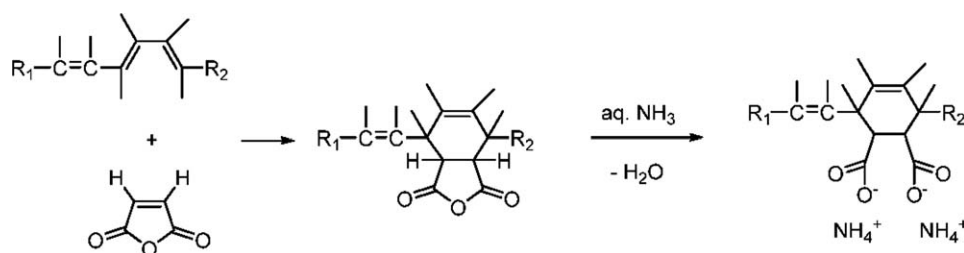
Penetration of the binders was measured with incident light fluorescence microscopy (Olympus BH2-RFCA, cube DMB and exciter filter 20BP490). The fluorescent light source was a 100 W Mercury lamp. The coated samples were stained with 1% of aqueous safranin solution to alter the autofluorescence of wood. After rinsing with water clear distinction, between stained wood and fluorescent binders could be seen exciting light near 490 nm. Measurements were done from cross sectional images. Face dressing of the samples was done with the razor blade. The samples were cut to size 20 mm  $\times$  20 mm  $\times$  7 mm.

The topography of the film surfaces was measured with PL $\mu$  2300 Optical Imaging Profiler 3D-profilometer. The binders were mixed with a cobalt drier with amount of 0.1 wt % content of cobalt prior film preparation. The binders were applied on pine sapwood. The first layer applied (77 g/m<sup>2</sup>) penetrated and the second layer applied (141 g/m<sup>2</sup>) formed a film. The film thickness varied between 17 and 50  $\mu\text{m}$ .

Water repellency property of the binders was evaluated by determination of contact angles of water. The instrument used for the contact angle measurements was CAM200 (KSV Instruments, Finland). Water droplets with the volume of 6–7  $\mu\text{L}$  were placed on the substrates and the static contact angles were recorded as a function of time (up to 600 s).



Scheme 1 Ene-reaction of isolated double bonds with maleic anhydride.<sup>16</sup>



**Scheme 2** D-A reaction of conjugated *cis*-double bond with maleic anhydride followed by ring opening and neutralization with aqueous ammonia.<sup>16</sup>

The chemical changes at the double bonds during curing were monitored with Fourier transform infrared spectroscopy (FT-IR) technique. The changes in the intensity of the  $3010\text{ cm}^{-1}$  peak (*cis*-H—C=C—H stretching) against an internal standard of  $2854\text{ cm}^{-1}$  peak ( $CH_2$  stretching) were monitored at certain intervals. Mid-infrared spectra were recorded by using a Fourier transform infrared spectrometer Bio-Rad FTS 6000 equipped with a KBr beam splitter. The spectrometer was equipped with Bio-Rad UMA 500 IR-microscope with MCT-detector (mercury-cadmium-tellurium). The spectra were recorded by using reflection technique and collected in the wave number range of  $4000\text{--}700\text{ cm}^{-1}$ . The spectra were measured from the early wood part of the sample.

## RESULTS AND DISCUSSION

### Preparation of maleated binders

In this study, the maleated hybrid binders were prepared via reaction of maleated TOFA and long oil alkyd resins. Two different types of binders were prepared by using two types of alkyd resins. The alkyds differed based on their fatty acid content and also by other composition. The common feature was the use of isophthalic acid as polybasic acid, because it gives alkyd resins higher stability.<sup>14</sup> One of the alkyds was TOFA-based, very long oil alkyd (oil length of 85%). Another alkyd was both TOFA and conjugated TOFA-based long oil alkyd with an oil length of 60%. TOFA was selected as fatty acid source because it has a unique fatty acid mixture containing small amount of saturated fatty acids and a high degree of unsaturated fatty acids.<sup>15</sup> The type of unsaturation influences the drying rate and double bond conjugation accelerates the oxidative drying process.<sup>16</sup> For this purpose, isomerization of TOFA to conjugated fatty acids was performed.

With the TOFA-based, long oil alkyds (Table I, alkyds 1 and 2) pentaerythritol was used as polyol as the neopentyl structure lends stability and the four equally reactive hydroxyl groups enables high degree of branching of the alkyd backbone.<sup>17,18</sup> With the second type of alkyd (Table I, alkyds 3 and 4),

trimethylolpropane was used in addition of pentaerythritol, because of the high functionality of pentaerythritol together with the use of conjugated fatty acids increases tendency for gelling. In addition, benzoic acid was used as monofunctional modifier, because it reacts with the growing polymer chain as chain-stopper. The characteristics of the alkyd resins made are summarized in the Table I.

Maleation of TOFA was carried out separately. The reaction of maleic anhydride with unsaturated fatty acids is well known.<sup>16,19–21</sup> With conjugated *cis*-double bonds, maleic anhydride reaction mechanism is Diels-Alder type, which proceeds exothermically. With isolated double bonds, higher temperatures are needed and reaction of maleic anhydride occurs at the allylic position via ene-reaction, forming a substituted succinic anhydride derivative (Schemes 1 and 2).<sup>16–21</sup>

The degree of maleation influences the binder dispersibility. Sufficient amount of acid groups are needed to make the resin dispersible; however, too high-acid values leads to limited hydrolytic stability. In this study, TOFA was treated with 6.5 wt % of maleic anhydride. Typical acid values obtained are given in Table II. The acid values increased with maleic anhydride modification, as expected. One product (MA TOFA 1) has somewhat smaller acid number than the other products. This might be caused by loss of maleic anhydride due to sublimation or decarboxylation.

The binders were prepared using two parts of the corresponding alkyd and 1 part of maleated TOFA, heating the components together at  $120^\circ\text{C}$  during 3 h, similarly as already reported in the literature.<sup>11</sup> Some of the acid functionality of the maleated TOFA

**TABLE II**  
Acid Values of Maleated TOFA

	Acid value (mg of KOH/g) <sup>a</sup>
MA TOFA 1	230
MA TOFA 2	243
MA TOFA 3	241

<sup>a</sup> Acid value of TOFA is 198.

TABLE III  
Maleic Anhydride Modified Binders Prepared

	Alkyd <sup>a</sup>	MA TOFA <sup>a</sup>	AV <sup>b</sup>	OH <sup>c</sup>	Viscosity (P)
Binder 1	1	3	86	16	3.2 <sup>d</sup>
Binder 2	2	1	84	–	1.2 <sup>e</sup>
Binder 3	3	2	85	26	6.8 <sup>d</sup>
Binder 4	4	1	93	–	1.3 <sup>d</sup>

<sup>a</sup> The number refers to the code of the alkyd and maleated TOFA used.

<sup>b</sup> Acid value (mg of KOH/g).

<sup>c</sup> Hydroxyl value (mg of KOH/g).

<sup>d</sup> Viscosity values determined at the temperature of 50°C.

<sup>e</sup> Viscosity values determined at the temperature of 75°C.

is consumed in the esterification reaction with alkyd hydroxyl groups; however, a sufficient amount of acid groups remain to stabilize the final binder.<sup>5</sup> The characteristics of the binders made are summarized in the Table III.

### Resin emulsification

Properties of emulsions depend upon large number of variables, such as properties of the dispersed resin and surfactants, as well as the emulsification technique and conditions.<sup>2–4,22</sup> Emulsions are subject to changes with a time and a prerequisite for good colloidal emulsion stability is that small droplets and a narrow droplet size distribution are obtained.<sup>2–4</sup>

Phase inversion is a process where a dispersion of drops of one liquid in another liquid inverts its morphology, i.e., the drops get together and become continuous phase, and the original continuous phase becomes dispersed as drops.<sup>2–4,23</sup> With this method, fine emulsions with small particle sizes can be obtained, and this method is typically used for emulsification of viscous resins as the resin can be easily heated up to a desired temperature.<sup>3,20,24</sup>

In this study, emulsions with solid content of 45 wt % were prepared by heating the resin up to 50°C and then, water was added dropwise into the resin. After this, the pH of the emulsion was set to value of 7, and then, the emulsion was additionally homogenized with high-shear homogenizer or the pH of the emulsion was further set to value 8.8 and no high-shear homogenization was performed. The increase in pH leads to an increase in the amount of carboxylate ions, and it is likely to affect on stability

of the emulsion. Within this study, both of the emulsion types were found to be stable. Aqueous ammonia (25 wt %) was used for neutralization and no organic co-solvents were used. The emulsion types prepared are summarized in the Table IV.

### Characterization of conjugated TOFA

The conjugation of the unsaturated fatty acids of TOFA was confirmed by proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H-NMR).<sup>10</sup> The reaction products were monitored for disappearance of linoleic acid. The signal associated with the methylene group between the two olefinic groups of linoleic acid should be absent (near 2.7 ppm) and the characteristic signals associated with the conjugated double bonds should be present (in the 5.3–6.3 ppm region).<sup>10</sup> Quantitative conversion of linoleic acid was attained as can be seen from the <sup>1</sup>H-NMR spectra of a representative example of the conjugated TOFA and the starting material TOFA (Figs. 1 and 2). The proton spectrum of TOFA was assigned as follows. The high-field region of the spectrum contains the methyl and methylene peaks at 0.88 ppm (–CH<sub>3</sub>), 1.24–1.45 ppm (–CH<sub>2</sub>–), 1.65 ppm (HOOC–CH<sub>2</sub>–CH<sub>2</sub>–), around 2.06 ppm (CH<sub>2</sub>–CH=CH), and 2.35 ppm (HOOC–CH<sub>2</sub>–). The characteristic peak associated with the methylene group between the two olefinic groups of linoleic acid appear at 2.77 ppm (–CH=CH–CH–CH=CH–). The peaks of the olefinic protons are observed around 5.35 ppm (–CH=CH–). The proton spectrum of the conjugated TOFA was assigned as follows. The high-field region of the spectrum contains the methyl and methylene peaks at 0.85 ppm (–CH<sub>3</sub>), 1.08–1.40 ppm (–CH<sub>2</sub>–), 1.60 ppm (HOOC–CH<sub>2</sub>–CH<sub>2</sub>–), around 1.93–2.18 ppm (CH<sub>2</sub>–CH=CH) and 2.30 ppm (HOOC–CH<sub>2</sub>–). The small peak observed at 3.63 ppm was assigned to polyethylene glycol residue. The peaks around 5–6 were assigned to the olefinic protons; 5.18–5.44 ppm (–CH=CH–), 5.59 ppm

TABLE IV  
MA Binder Emulsions

	Binder	pH	Emulsification
Emulsion 1	1	8.8	Low shear
Emulsion 2	2	7.0	High shear
Emulsion 3	3	8.8	Low shear
Emulsion 4	4	7.0	High shear

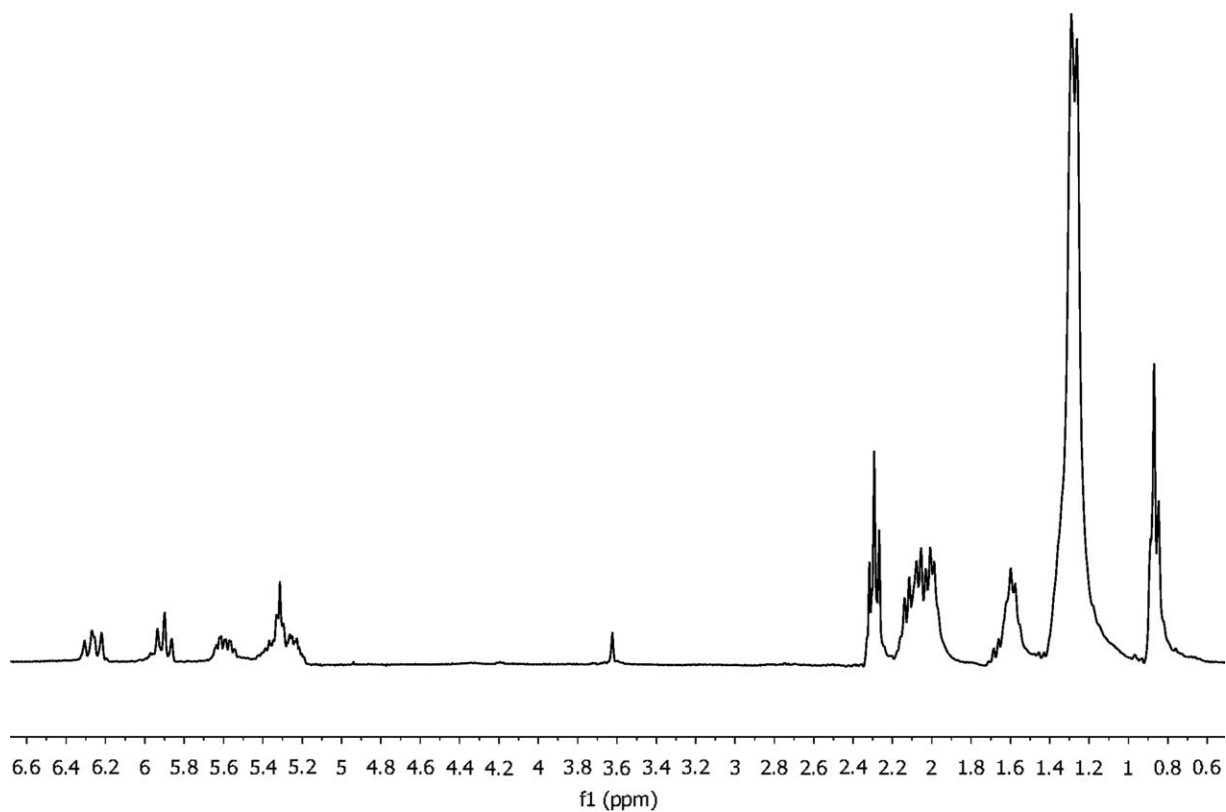


Figure 1 <sup>1</sup>H-NMR spectrum of a representative sample of isomerization product.

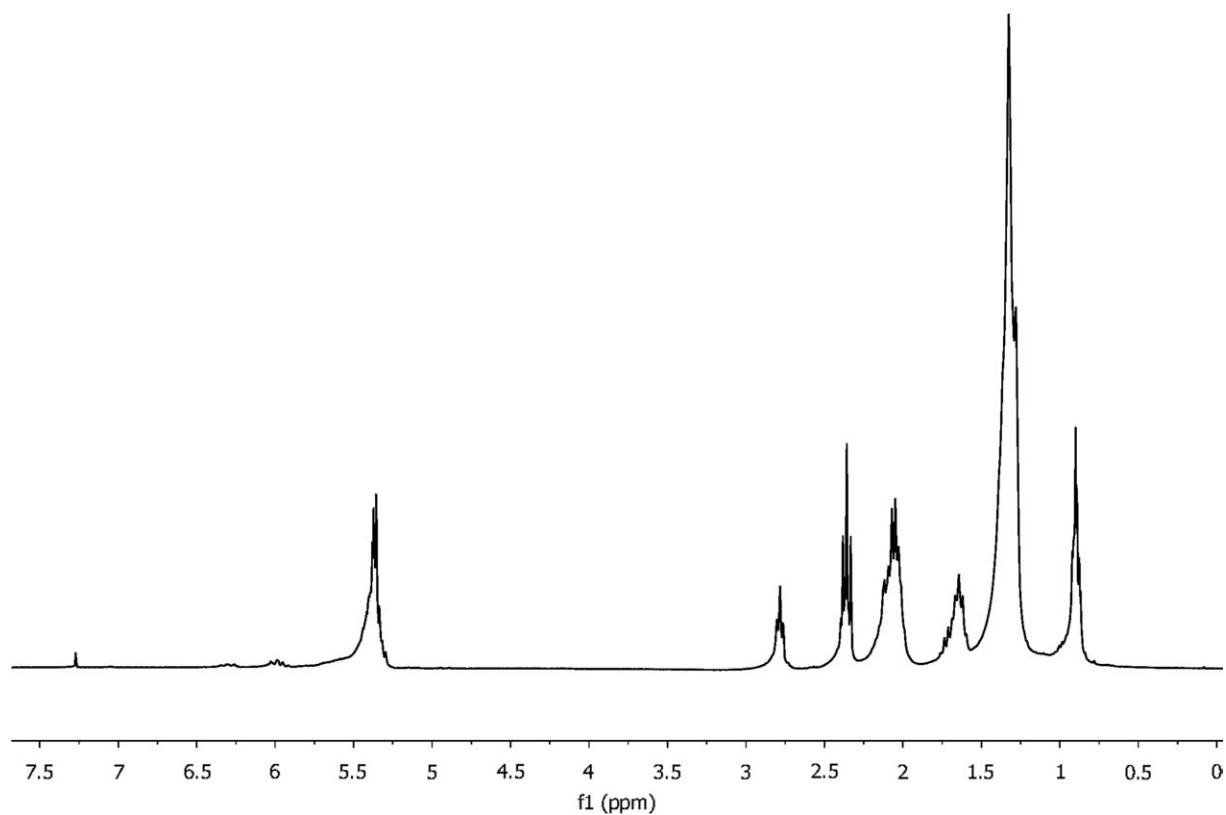


Figure 2 <sup>1</sup>H-NMR spectrum of TOFA.

TABLE V  
GPC Results

	$M_w$
Alkyd 1	25,988
Alkyd 3	16,372
Binder 1	22,565
Binder 3	16,686

( $-\text{CH}=\text{CH}-$ ), 5.90 ppm ( $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$ ) and 6.26 ppm ( $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$ ).

### Molecular weight

Molecular weight (weight average  $M_w$ ) of representative samples of alkyd resins (alkyds 1 and 3) and maleated binders (binders 1 and 3) were measured by GPC (Table V). Broad molecular weight distributions were detected as typical for alkyd resins. Similar profiles were observed also with the maleated binders. The alkyd 1 has somewhat broader molecular weight distribution compared with the alkyd 3, which is in harmony with the fact that the alkyd 1 has higher degree of branching due to use of pentaerythritol and the latter is chain stopped alkyd. The same trend was observed with maleated binders originating from the two alkyd resins used.

### Penetration studies on wood substrate

Penetration is an important factor for the durability of a coating, and thus for the protection of the wood.<sup>25</sup> In this study, the penetration depth of the binders synthesized was measured with aid of fluorescence microscopy. First, penetration of emulsions 2 and 4 were compared with the references of WB1 and WB3 (Table VI). The emulsions 2 and 4 were prepared with the same method. Wood substrates were pine heartwood and sapwood, as well as spruce heartwood and sapwood. Subsequently,

TABLE VI  
Binder Amount Applied and the Observed Penetration Depth

Binder	Substrate	Amount (g/m <sup>2</sup> )	Penetration (μm) <sup>a</sup>
Emulsion 2	Pine sapwood	95	155
	Pine heartwood	77	109
	Spruce sapwood	81	102
	Spruce heartwood	93	143
Emulsion 4	Pine sapwood	85	155
	Pine heartwood	90	99
	Spruce sapwood	88	132
	Spruce heartwood	105	139
WB1	Pine sapwood	80	91
WB3	Pine sapwood	121 <sup>b</sup>	124

<sup>a</sup> Deepest penetration.

<sup>b</sup> Two layers applied.

TABLE VII  
Binder Amount Applied and the Penetration Depth of the Diluted Samples

Binder	Substrate	Amount (g/m <sup>2</sup> )	Penetration (μm) <sup>a</sup>
Emulsion 1	Pine	141	102
	Spruce	201	140
Emulsion 3	Pine	121	83
	Spruce	156	108
WB2	Pine	111	78
	Spruce	193	99

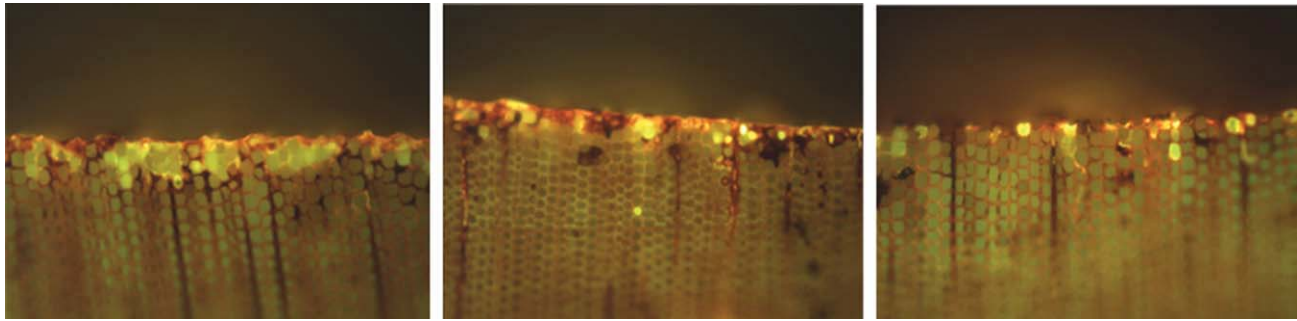
<sup>a</sup> Deepest penetration.

measurements were made with emulsions 1 and 3 and the reference of WB2. All the samples were diluted to solid content of 23%. A cobalt drier was added to all samples with amount of 0.1 wt % of cobalt calculated from the solid content of the binder. The binders were applied in one layer by brush on pine and spruce substrate. The binder amount applied and the observed penetration depth of the samples is listed in the Table VII.

Regarding the average penetration on pine sapwood, the penetrations of the emulsions 2 and 4 were somewhat higher (155 μm) than with the reference WB3 (124 μm) and WB1 (91 μm). No clear difference between the emulsions 2 and 4 was noticed even with other substrates.

With the emulsions 1 and 3, the penetrations were also somewhat higher (102 and 83 μm) than with the reference alkyd emulsion (78 μm, WB2) on pine substrate. Similar results were obtained with spruce; the penetration depth of the binders synthesized was as deepest 140 and 108 μm, whereas the penetration depth of the reference was 99 μm. The penetration of emulsion 1 was somewhat higher than with emulsion 3, which is in harmony with the assumption, that the binder based on alkyd 1 dry somewhat slower (TOFA-based, very long oil alkyd) and thus, it has time to penetrate higher. However, the difference between the binder types was not so obvious with the emulsions 2 and 4. Overall, the penetration of emulsions 2 and 4 was somewhat higher than with emulsions 1 and 3.

However, the differences were not very large and it is difficult to draw conclusions on the binder types simply based on this study. The penetration depth depends on the binder amount applied and is affected by the properties of the binders, such as molecular weight, solid content, viscosity, surface tension, and drying rate, as well as is affected by the wood species and its surface texture. However, it can be concluded that the binders synthesized have penetration properties comparable or even better than with the commercial binders used as reference. In the Figure 3 is presented representative images of the penetration studies on pine substrate.



**Figure 3** Fluorescence microscopy images of emulsions 1 and 3, and WB3 on pine substrate (image on the left hand side is emulsion 1, the image in the middle is emulsion 3, and on the right hand side is WB3). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

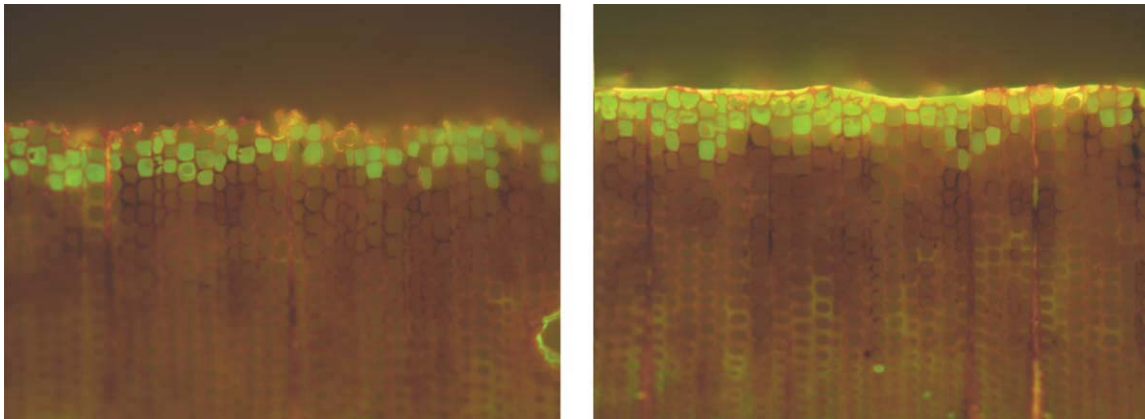
### Film surface topography

Film formation and surface topography of emulsions 2 and 4 was studied. Two layers of the binder were applied on pine sapwood. The first layer applied penetrated and the second layer applied formed a film. The film thickness varied between 17 and 50  $\mu\text{m}$ . Figure 4 shows representative images (emulsion 2) obtained by fluorescence microscopy. The roughness of the film surface was evaluated with optical 3D-pro-

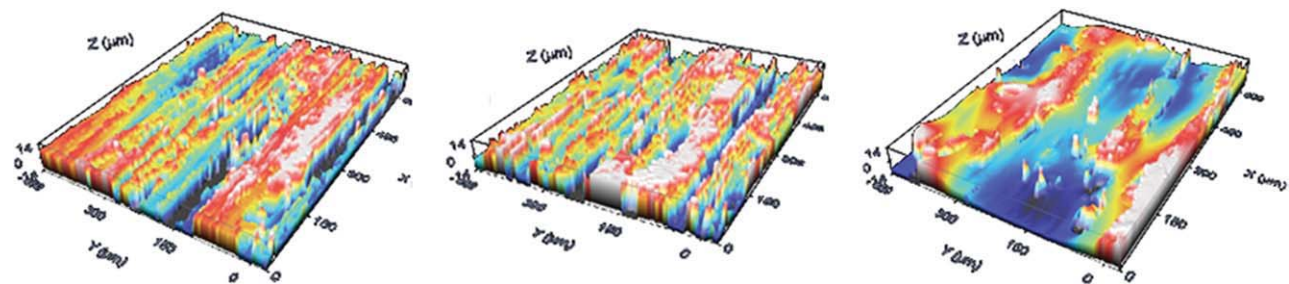
filometer. Images of the surface topography show that two layers of the coating provided a fairly smooth and crack-free film (Fig. 5).

### Water repellency and contact angle measurements

The water repellency of two representative binders (emulsions 2 and 4) was evaluated by measuring the contact angle of water on the coated substrates.

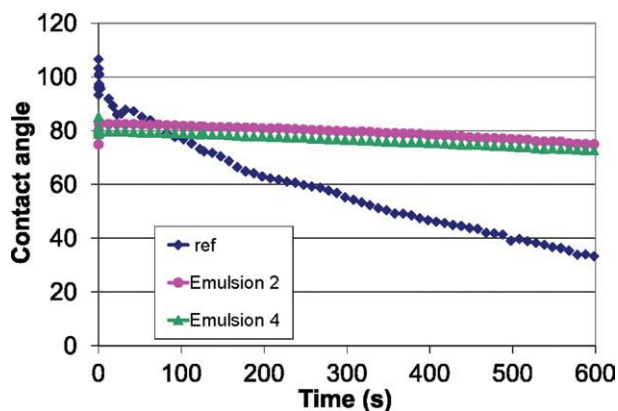


**Figure 4** Fluorescence microscopy images of emulsion 2 (image on the left hand side is coated with one layer and the image on the right hand side is coated with two layers). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5** Surface topography images of emulsion 2 (image on the left side is substrate without coating, in the middle is the image with one coating layer and on the right side is two layers coat). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 6** Contact angle of water on coated wood and on uncoated reference. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

High values of contact angle indicate good hydrophobic nature of coating, whereas low values indicate that water wets the surface. The contact angles of a drop of water placed on coated wood substrates and uncoated reference were measured for period of 10 min (600 s). Contact angle of water on binder coats had much higher values (between 80 and 70) than on uncoated reference (Fig. 6). According to this study, the binders synthesized have hydrophobic, water repellent properties. There were no differences detectable between the two binders.

### Reactions of double bonds during drying

Drying of an alkyd emulsion involves evaporation of water, coalescence of droplets, oxygen uptake, and cross linking as a result of radical reactions at the unsaturated fatty acid chains leading to final polymer network and to the cured film. These oxidation reactions are slow and the drying time of alkyd

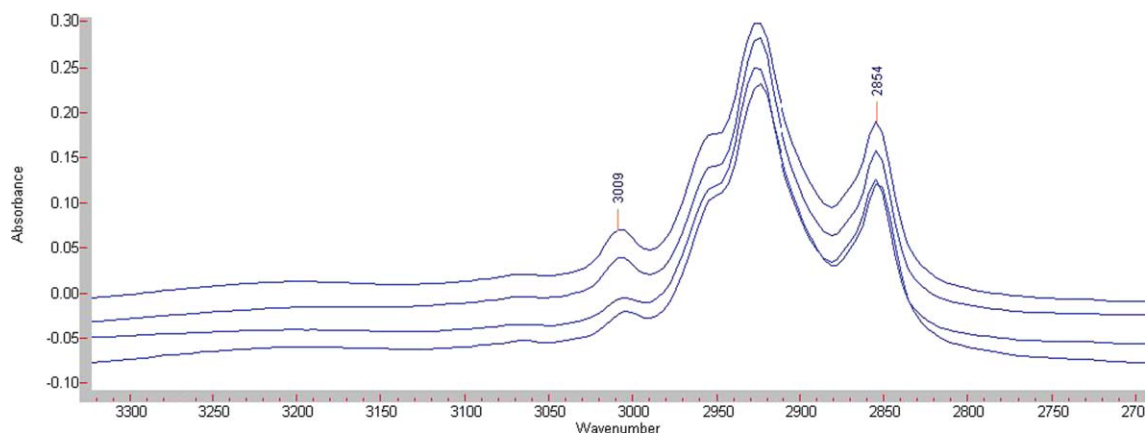
paint would be over 24 h without use of siccatives, which accelerate the rate of cross linking.<sup>26</sup>

With this study, the aim was to study the chemical changes at the double bonds during cross linking with FT-IR technique by monitoring the intensity of a characteristic peak at  $3010\text{ cm}^{-1}$  (*cis*-C=C-H stretching). The peak will become smaller as the autoxidation reaction goes forward. One sample (emulsion 3) was compared with the reference of WB2. With the binder synthesized, the chemical changes at the double bonds were detectable within 22 h (Fig. 7), although, the intensity of the changes was not high. There were no detectable changes with the reference alkyd emulsion within the observation period. It is obvious that a shorter drying time would be desirable and, however, it should be noted that the drying system and formulation was not optimized.

### CONCLUSIONS

In this article, we presented our studies on preparation of self-emulsifying binders and properties thereof. The binders were prepared by reaction of long oil alkyd resins with maleated derivatives of fatty acids. These binders were dispersed in water without use of external surfactants and free from volatile organic compounds. The binders were evaluated based on their performance properties, including penetration, film formation, and water repellency property against commercial references.

The difference between the penetration depths between the binders synthesized was not very large and it is difficult to draw conclusions on the binder types based on the penetration. However, according to this study, the binders synthesized have penetration properties comparable or even better than with the commercial binders used as reference. The water contact angle measurements showed that the binders



**Figure 7** FT-IR spectra taken at time period of 0 h, 3.5 h, 22 h, and 46 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

have hydrophobic, water repellent properties. The surface topography study showed that two layers of the binder provide a fairly smooth and crack-free film.

According to these results, binders with interesting properties have been prepared. It is believed that such binders would be useful, e.g., for priming applications, where good penetration and water repellent properties are critical characteristics.

The authors thank M. Löijä and S. Eskonniemi for the molecular weight determinations and FT-IR assistance.

## Reference

1. Aigbodion, A. I.; Okieimen, F. E.; Obazee, E. O.; Bakare, I. O. *Prog Org Coat* 2003, 46, 28.
2. Bakker, P.; Klijn, T.; Baltussen, J. J. M.; Bolin, M. *Färg och Lack Scandinavia* 2004, 5, 4.
3. Weissenborn, P. K.; Motiejauskaitė, A. *Prog Org Coat* 2000, 40, 253.
4. Östberg, G.; Bergenståhl, B.; Huldén, M. *Colloids Surf A* 1995, 94, 161.
5. Nakayama, Y. *Prog Org Coat* 1998, 33, 108.
6. Holmberg, K. *Prog Org Coat* 1992, 20, 325.
7. Hellgren, A. C.; Weissenborn, P.; Holmberg, K. *Prog Org Coat* 1999, 35, 79.
8. Zückert, B.; Biemann, H. *Färg och Lack Scandinavia* 1993, 2, 29.
9. Uschanov, P.; Heiskanen, N.; Mononen, P.; Maunu, S. L.; Koskimies, S. *Prog Org Coat* 2008, 63, 92.
10. Reaney, M. J. T.; Jones, S.; Westcott, N. D. WO Pat. 0,151,597 (2001).
11. Nakayama, Y. *Jpn Pat* 63,251,479 (1988).
12. Aihara, T.; Nakayama, Y.; Umeyama, K.; Sawada, K.; Shinohara, M. U.S. Pat. 4,436,849 (1984).
13. Dhein, R.; Schoeps, J.; Küchenmeister, R. U.S. Pat. 4,346,044 (1982).
14. Oldring, P. K. T., Ed. *Resins for Surface Coatings, Alkyds and Polyesters*, 2nd ed.; Wiley: London, 2000; Vol. 2, p 43.
15. Hase, A.; Pajakkala, S. *Lipid Technol* 1994, 6, 18.
16. Bentley, J. In *Paint and Surface Coatings Theory and Practice*; Lambourne, R., Ed.; Ellis Horwood Ltd.: Chichester, UK, 1987; p 41.
17. Lin, K. F. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kvoschwitz, J. L., Ed.; Wiley: New York, 1991; Vol. 2, p 59.
18. Available at: [http://www.perstorp.com/upload/pentaerythritol\\_20081124.pdf](http://www.perstorp.com/upload/pentaerythritol_20081124.pdf) (Accessed on December 8, 2009).
19. Williams, R. C. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Kvoschwitz, J. L., Ed.; Wiley: New York, 1985; Vol. 12, p 300.
20. Metzger, J. O.; Biermann, U. *Fat Sci Technol* 1994, 96, 321.
21. Sastry, G. S. R.; Murthy, B. G. K.; Aggarwal, J. S. *J Am Oil Chem Soc* 1970, 48, 686.
22. Salager J. L. In *Surfactants in Solution, Surfactants Science Series 64*; Chattopadhyay, A. K., Ed.; Marcel Dekker: New York, 1996; Chapter 16, p 261.
23. Zambrano, N.; Tyrode, E.; Mira, I.; Marquez, L.; Rodríguez M.-P.; Salager, J.-L. *Ind Eng Chem Res* 2003, 42, 50.
24. Fernandez, P., André, V.; Rieger, J.; Kühnle, A. *Colloids Surf A* 2004, 251, 53.
25. Van den Bulcke, J.; Rijckaert, V., Van Acker, J.; Stevens, M. *Holz als Roh- und Werkstoff* 2003, 61, 304.
26. Van Gorkum, R.; Bouwman, E. *Coord Chem Rev* 2005, 249, 1709.