Modified Syntheses of Ca-Resinates by Fusion Method

S. Sundqvist, S. Turunen, and E. Paatero
Laboratory of Industrial Chemistry, Lappeenranta University of Technology, FIN-53851 Lappeenranta, Finland

F. Twigt
Arizona Chemical, 8000 AC Zwolle, The Netherlands

Tall oil rosin was modified with fumaric acid or maleic acid anhydride to get fortified rosin, which was used as a raw material in fusion Ca-resinate syntheses. Two reaction steps were observed in the syntheses. A fast resination reaction takes place at 235°C, and a slow decarboxylation of rosin acids forms neutral rosin oil at 265°C. A mechanistic model for the decarboxylation reaction step was derived to explain the effect of fortifying substances on the reaction kinetics. A multivariate calibration method using partial least-square (PLS) regression was applied to monitor the acid concentration decrease on the basis of infrared spectroscopic data during the fortified syntheses. A mixture of unmodified rosin and rosin oil (decarboxylated rosin) was used as a raw material in a novel modification of fusion syntheses to increase the mass yield of the resinate. In the modified rosin oil syntheses, decarboxylation of rosin acids is avoided, and recycling the added rosin oil considerably improves the mass yield of the resinate syntheses.

Introduction

Resinates are polyvalent metal salts of rosin acids. Ca- and Ca/Mg-resinates are used as binders in gravure inks for printing, and solution viscosity is an important quality specification of resinates to be used as an ink vehicle. In modified resinate syntheses, rosin is generally fortified by reacting it with a dienophile, such as maleic acid or maleic acid anhydride or fumaric acid. The reaction products are tricarboxylic acids, which are referred to as maleopimaric or fumaropimaric acids. The rosin adducts have high melting points, and the acidity makes them reactive with metal hydroxides to form resinates with improved printing qualities.

The aim of this article is to study modified resinate syntheses in order to determine the effect of rosin acid fortification on reaction kinetics. A multivariate calibration model is applied to modified resinate syntheses to avoid difficult sampling in monitoring the complex resinate synthesis using fortified rosin as a raw material. In addition, in this article a new modification of fusion resinate synthesis using rosin oil addition is introduced. The new synthesis method is developed to increase the mass yield of the synthesis and to adjust the viscosity of the resinate to the desired level to be used in the printing ink industry.

In fusion resinate syntheses, a nonlinear solution viscosity increase causes problems in monitoring and controlling the resinate process. The direct resination reaction (Figure 1) is complete at 235°C in a few minutes (Sundqvist et al., 1999b), but the reaction cannot be carried out to the desired viscosity level due to the blocking of the unreacted $Ca(OH)_2$, as described by different authors (Petrone, 1971; Jilek, 1976; Oldring and Hayward, 1987).

For this reason, the viscosity is often raised to the required level at an increased reaction temperature (265°C) to enable the thermal decarboxylation of rosin acids to take place. In the decarboxylation reaction step, volatile neutral rosin oil is formed (Figure 2). The rosin oil evaporates from the synthesis, causing about 30% mass loss from the system. Thus, the

---

Correspondence concerning this article should be addressed to S. Sundqvist.
Current address of F. Twigt: Avery Dennison, 2300 AA Leiden, The Netherlands.

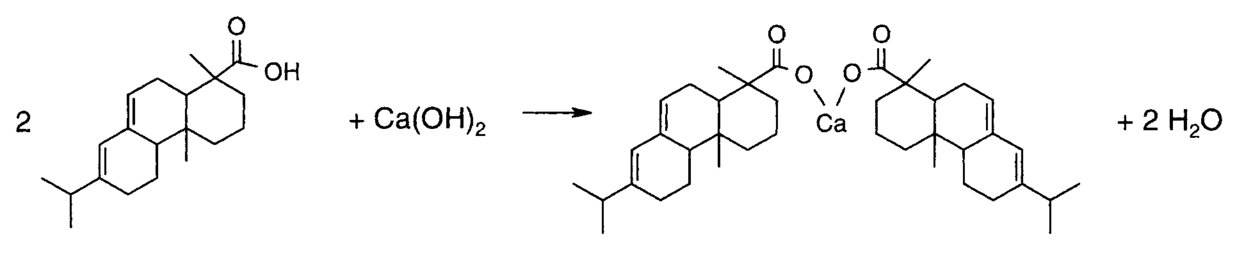


Figure 1. Resination reaction.

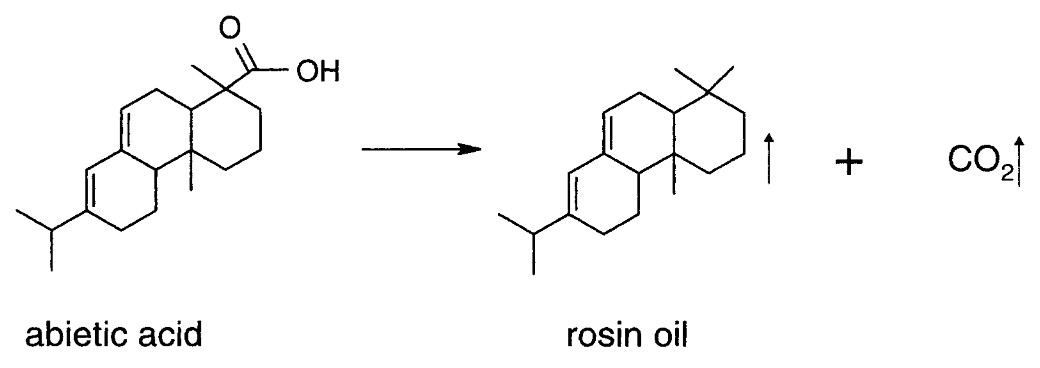


Figure 2. Decarboxylation reaction.

resinate concentration in the reactor increases during the decarboxylation reaction step, and the target viscosity of the product can be obtained. However, such a loss of raw material (rosin) is undesirable for economic reasons.

It is not easy to keep the nonlinear viscosity increase under control without knowing the kinetics of the decarboxylation reaction. In our previous study (Sundqvist et al., 1998), a semi-empirical viscosity model was derived to monitor and predict the solution viscosity increase during the fusion resinate process. The simplified kinetic model for the synthesis was deduced based on acid-value measurements. Later (Sundqvist et al., 1999b) the kinetic model was verified by taking into account the mechanism of the thermal decarboxylation reaction. The reaction mechanistic studies were based on FTIR spectroscopic data analyses after the calibration problems of the complex reaction system were solved. The mechanistic model was derived for the Ca-resinate synthesis using unmodified rosin as the raw material.

In fusion resinate synthesis, rosin modification is often done by using fumaric acid (FA) or maleic acid anhydride (MAA) as fortifying substances. The use of FA or MAA increases the rosin acid functionality (Figure 3), and therefore affects the mechanism of the resination reaction and the decarboxylation reaction. In the present study, the effect of rosin acid modifications on reaction kinetics is studied and a kinetic model for the decarboxylation in fortified syntheses is derived. FTIR analyses are carried out to measure the resinate concentration, free rosin acid concentration, and the anhydride concentration of the complex reaction mixture. The total acid content is determined based on acid value titration, and thus the amount of rosin acids solvating the resinate molecules is calculated. The solvation phenomenon during resinate syntheses was observed in our previous study (Sundqvist et al., 1999b).

The multivariate calibration methods combined with IR analyses were previously applied (Sundqvist et al., 1999a) for

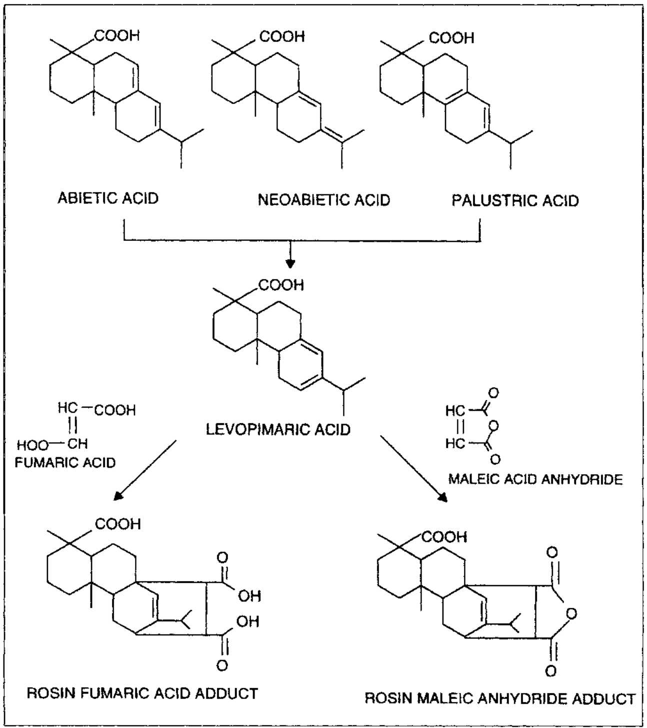


Figure 3. Fortification reactions of rosin acids.

the viscosity monitoring of the modified syntheses (industrial Ca/Mg-resinate samples). The aim of the derivation of multivariate calibration models for fortified resinate syntheses is to avoid analytical and sampling problems of the complex resinate reaction mixture. In this article PLS calibration models are derived for the modified Ca-resinate syntheses using different amounts of FA and MAA in order to monitor the acid value during the syntheses. The models can be used for both the kinetic studies of modified resinate syntheses and on-line process monitoring.

In traditional fusion resinate syntheses at 265°C, the target viscosity for the product is obtained during the decarboxylation reaction step. When decarboxylated rosin (that is, rosin oil) evaporates from the system, the resinate concentration increases. Consequently, the mass yield of the synthesis decreases. In this study, however, in order to get improved mass yield, the resinate syntheses are carried out with rosin oil additions at 235°C. The thermal decarboxylation is avoided by the lower reaction temperature. The addition of rosin oil to the reaction mixture enables further resination reaction with a higher degree of neutralization of rosin acids than in traditional syntheses. Due to the higher resinate concentration in the reaction mixture, the solution viscosity of the resinates will increase to the desired level when the added rosin oil is evaporated. The mass yield of the rosin oil modified syntheses can be as high as 100% because it is possible to recycle the added rosin oil in the reaction mixture.

Experimental Studies

Fortified syntheses

The same experimental setup as in our previous study (Sundqvist et al., 1999b) was used for the Ca-resinate syntheses. The syntheses were carried out in a 300-mL glass reactor and the reaction mixture was stirred with a four-blade impeller. The temperature was controlled with an electrical muff. The system was purged with a constant nitrogen flow to apply an inert atmosphere. The rosin (acid value = 163 mg(KOH)/g) used as a raw material in Ca-resinate synthesis was fortified by adding FA or MAA to the rosin melt at 195°C. The aliquots of the fortification substances were 2, 4, and 6 wt. % of the rosin amount. The reaction time in fortifying the rosin was 2 h.

After the fortification reaction, the temperature was raised to 235°C, and $Ca(OH)_2$ was added into the reaction mixture. The $Ca(OH)_2$ addition was equal to the amount required to obtain the theoretical target acid value of 70 mg(KOH)/g calculated for the resinate without fortification. After the resination reaction was complete (in about 15 min), the temperature was raised to the final reaction temperature (265°C), and the reaction time was 5 h.

Syntheses with rosin oil additions

In the syntheses with rosin oil additions, the mixture of rosin oil [acid value = 25 mg(KOH)/g] and rosin was heated to 235°C. The rosin oil additions were 0, 20, 30, and 40 wt. % of the rosin amount. The reaction time after the addition of $Ca(OH)_2$ was 30 min. The amount of added salt was equal to the amount required to obtain the theoretical target acid values of 0, 25, 50, 70, and 90 mg(KOH)/g calculated for the product.

Analyses

The complex reaction mixture was analyzed by acid value titration and FTIR measurements. The potentiometric acid value titration was carried out with a Mettler Toledo DL25 Titrator using a DG111-SC electrode. The sample was diluted in toluene, and an equal volume of technical alcohol was added to the solution. The titration was done using 0.2 M potassium hydroxide. In the potentiometric titration of fortified rosin and resinate, two equivalent points were recorded. In the first equivalent point, half of the anhydride is considered to be esterified by ethanol and the other half reacts with KOH (Zinkel et al., 1989). Therefore, the acid concentration of fortified resinates was calculated based on the total consumption of the titer corrected by the titrated anhydride amount.

A Perkin-Elmer 2000 Infra-Red-Spectrophotometer equipped with a CaF_2 transmission cuvette (0.05 mm) was used to measure the resinate concentration and the concentration of the free rosin acids capable of associating to dimers in toluene. The sample was 15 wt. % toluene solution of the resinate. The calibration for the FTIR analyses was carried out in our previous study using abietic acid and Ca-abietate as standards (Sundqvist et al., 1999b). In addition, a new calibration was made using MAA fortified rosin as a standard for the anhydride concentration in the resinate reaction mixture.

Results and Discussion

Fortified syntheses

Mass-Balance Calculations. The effect of the fortifying substances on the composition of the resinate reaction mixture was studied. The mass balance of the fortified syntheses was calculated by regarding the resinate amount as constant after the resination reaction has been completed and the temperature raised to 265°C. Thus, the increase in the resinate concentration during decarboxylation indicates the relative mass loss of the system, and the loss can be calculated according to Eq. 1, which is derived from the mass-balance equation:

$$\Delta m_{rel} = 1 - m_2/m_1 = 1 - c_1/c_2, \qquad (1)$$

where c_1 and c_2 denote the resinate concentrations in mol/kg, and m_1 and m_2 denote the masses of the reaction mixture at the reaction times t_1 and t_2, respectively. Based on mass-balance calculations, which are discussed in more detail in our previous study (Sundqvist et al., 1999b), a decarboxylated amount of fortified rosin was calculated during the syntheses.

General Progress of the Syntheses. In the fortified resinate syntheses, it was observed that the amount of decarboxylated rosin acid is greater in fumaric-acid-modified resinate syntheses than in maleic acid anhydride modifications (Figure 4). This is partly explained by the greater amounts of acid groups in fumaric acid modifications. The average decarboxylation

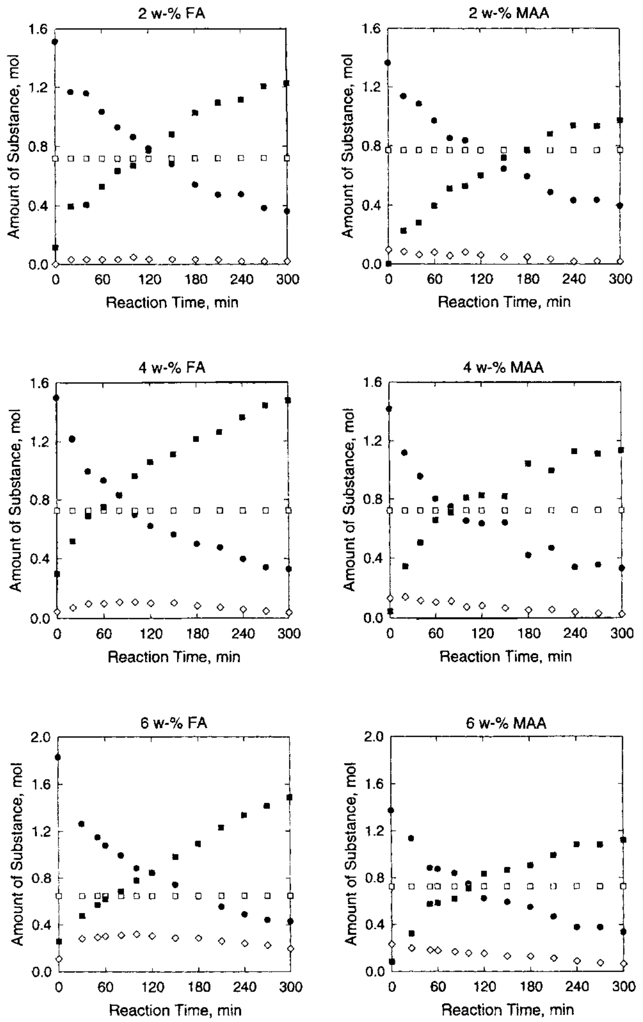


Figure 4. Mass corrected amount of substances in resinate syntheses modified with FA and MAA.

● Total acids; □ resinate; ◇ anhydride; ■ decarboxylated rosin.

degree of rosin acids during the 5-h reaction time was 87% for FA-modified syntheses and 78% for MAA-modified syntheses. The value was 81% for the reference synthesis without fortification.

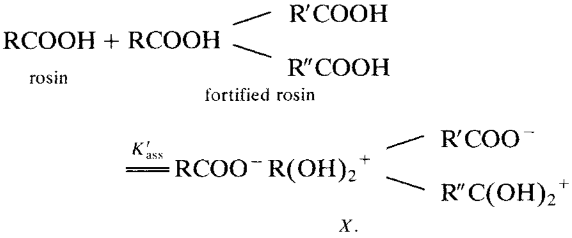
Kinetic Modeling of the Decarboxylation. The previously published mechanism for the rosin acid decarboxylation in the reaction mixture is based on the different reaction steps of solvating and free rosin acids analyzed by FTIR (Sundqvist et al., 1999b).

In the fortified resinate syntheses, the ratio between the free rosin acid concentration and the resinate concentration was compared to the same concentration ratio during unfortified reference synthesis. Figure 5 shows that the fortified rosin acids groups are free to associate to dimers in toluene solution analyzed by FTIR.

For the free rosin acids, RCOOH, the following protolysis equilibrium of the ion-pair formation is considered:

$$\mathrm{RCOOH} + \mathrm{RCOOH} \overset{K_{ass}}{\rightleftharpoons} \mathrm{RC(OH)_2}^+\,\mathrm{RCOO}^-. \tag{2}$$

In the case of fortified rosin acids, the number of acid groups is three (Figure 3). Therefore, the assumed equilibrium for the free acids becomes:



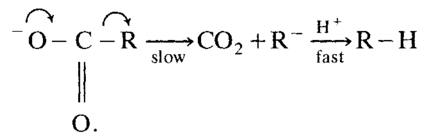
$$\underset{\text{rosin}}{\mathrm{RCOOH}} + \mathrm{RCOOH} \left\langle \begin{array}{l} \mathrm{R'COOH} \\ \mathrm{R''COOH} \end{array} \right. \text{fortified rosin}$$

$$\overset{K'_{ass}}{\rightleftharpoons} \mathrm{RCOO^-R(OH)_2}^+ \left\langle \begin{array}{l} \mathrm{R'COO^-} \\ \mathrm{R''C(OH)_2}^+ \end{array} \right. \quad X. \tag{3}$$

The quasi-equilibrium approximation is applied to this rapid step (Eq. 3) to express the concentration of the ion pairs X:

$$c_x = K'_{ass} c^4_{RCOOH}. \tag{4}$$

The decarboxylation of a carboxylate ion, RCCO$^-$, is generally believed to involve a carbanion intermediate (R$^-$) that subsequently acquires a proton from the solvent, or from another source (Sykes, 1986):



$$^-\mathrm{O-\underset{\underset{\displaystyle O.}{\|}}{C}-R} \xrightarrow[\text{slow}]{} \mathrm{CO_2} + \mathrm{R}^- \xrightarrow[\text{fast}]{\mathrm{H}^+} \mathrm{R-H} \tag{5}$$

In the case of free rosin acid decarboxylation, the proton is available in ion pairs, and the delocalized structure of the solvating rosin acids is the proton source in the decarboxylation of solvating acids.

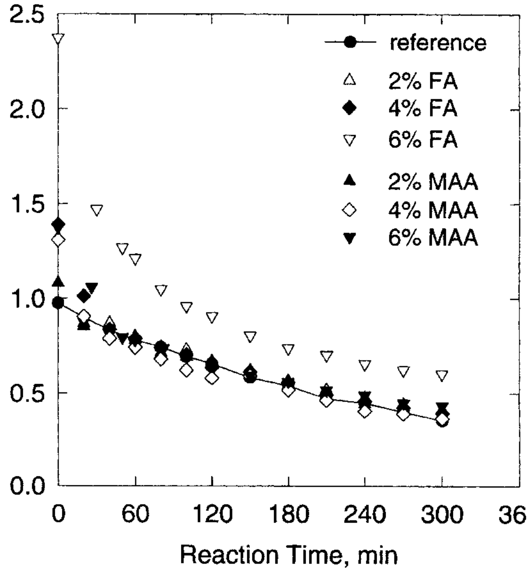


Figure 5. Ratio of free rosin acid concentration to resinate concentration in fortified resinate syntheses.

The reference synthesis was carried out without fortification.

Loss of carbon dioxide is normally the rate-limiting step, and the subsequent proton abstraction is rapid (Sykes, 1986). So the rate law for decarboxylation becomes

$$r_{\mathrm{deca}} = k'' c_{\mathrm{RCOO}^-}. \tag{6}$$

By taking Eq. 4 into account and assuming that the solvating rosin acids decarboxylate according to first-order kinetics, with respect to the rosin acid, the total decarboxylation rate of fortified rosin acids becomes

$$r_{\mathrm{deca}} = k_1 c_{\mathrm{RCOOH(s)}} + k_2 K'_{\mathrm{ass}} c^4_{\mathrm{RCOOH(f)}}, \tag{7}$$

where k_1 and k_2 denote the decarboxylation rate constants for the solvating forms of the rosin acids, RCOOH(s), and for the free acids, RCOOH(f), respectively; and K'_{ass} is the equilibrium constant of the ion-pair association of fortified rosin.

The reaction-rate parameters are estimated separately according to the partial reaction-rate equations (Eq. 8) for the solvating and the free rosin acids [i = RCOOH(s), RCOOH(f)]. The overall rate equation (Eq. 9) for decarboxylation is presented by means of partial reaction kinetics:

$$r_i = -\frac{1}{m}\frac{dn_i}{dt} = k_i c_i^{\alpha_i} \tag{8}$$

$$r_{\mathrm{deca}} = r_{\mathrm{RCOOH(s)}} + r_{\mathrm{RCOOH(f)}}. \tag{9}$$

The kinetic parameters were estimated from the differential equations (Eq. 8) using the Simflex algorithm, which is based on the simplex method introduced by Spendley et al. (1962). The differential equations were solved by means of linear multistep methods implemented in ODESSA, which is based on the LSODE software (Hindmarsh, 1983). The methods are also available in the MODEST software (Haairo, 1994).

The best kinetic models are obtained, with the parameter values α and k, as shown in Tables 1 and 2. The apparent reaction orders for total rosin acid decarboxylation depend on the amount of the fortifying substance used. Figure 6 shows that the kinetic model with the deduced reaction mechanism is well fitted to the analytical data.

The explanation degree of the kinetic model was over 90% in almost all of the data sets (Table 1). The scattering in the data (Figure 6) compared to the model line is mostly due to difficulties in sampling and analyzing the complex reaction mixture. A statistical error estimation of the syntheses would have required repeated experiments. But as the main aim of this study was to find general decarboxylation reaction mechanisms, that is, reaction orders for the free, solvating, and total rosin acids during the modified resinate syntheses, parallel syntheses were not carried out.

Table 1. Reaction Orders Estimated by the Kinetic Model, Eq. 8, and Explanation Degrees of the Model (R2-Values) in Fortified Resinate Syntheses

Amount of FA/MAA (wt. %)	Total Acids		Free Acids		Solvating Acids	
	Reaction Order	R2 %	Reaction Order	R2 %	Reaction Order	R2 %
2.0 FA	1.5	96	4.0	84	1.0	93
4.0 FA	2.0	99	4.0	94	1.0	95
6.0 FA	2.5	97	4.0	99	1.0	66
2.0 MAA	1.5	98	4.0	94	1.0	97
4.0 MAA	2.0	91	4.0	90	1.0	91
6.0 MAA	2.5	98	4.0	95	1.0	88

Table 2. Reaction-Rate Parameters for the Total Decarboxylation Reaction and Partial Reactions for Free Acids and Solvating Acids in the Fortified Resinate Syntheses

Amount of FA/MAA (wt. %)	Reaction-Rate Parameter $(\mathrm{mol/kg})^{1-\alpha}\cdot\mathrm{min}^{-1}$		
	Total Acids	Free Acids	Solvating Acids
FA 2.0	5.28×10^{-3}	1.78×10^{-2}	5.96×10^{-3}
FA 4.0	6.48×10^{-3}	1.82×10^{-2}	7.98×10^{-3}
FA 6.0	4.66×10^{-3}	3.48×10^{-2}	8.73×10^{-3}
MAA 2.0	4.83×10^{-3}	1.45×10^{-2}	6.52×10^{-3}
MAA 4.0	6.54×10^{-3}	2.09×10^{-2}	7.45×10^{-3}
MAA 5.0	5.71×10^{-3}	1.59×10^{-2}	6.01×10^{-3}

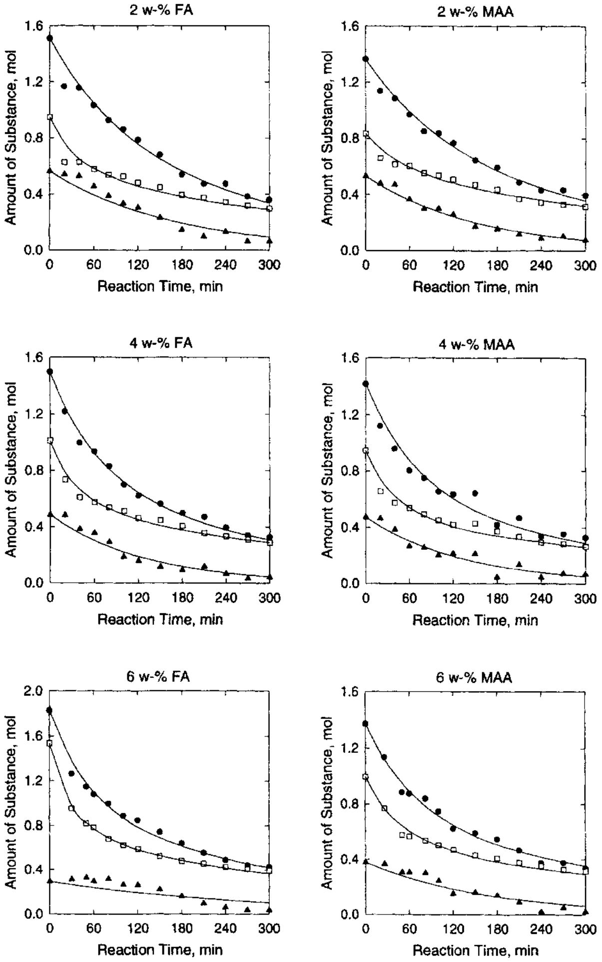


Figure 6. Application of the kinetic model, Eq. 8, to the decarboxylation reaction of the fortified rosin.

● Total acids; □ free acids; ▲ solvating acids.

Table 3. Optimal Number of Latent Variables in Different Calibrations of Acid Concentration in Fortified Ca-Resinate Syntheses by the Fusion Method*

Calibration Set	Test Set	No. of Latent Variables
4.0 wt. % FA	(I) 2.0 wt. % FA (II) 6.0 wt. % FA	3
4.0 wt. % MAA	(I) 2.0 wt. % MAA (II) 6.0 wt. % MAA	2
2/3 of FA data (randomized)	1/3 of FA data	4
2/3 of MAA data (randomized)	1/3 of MAA data	5

*The calibration is based on FTIR spectroscopic data.

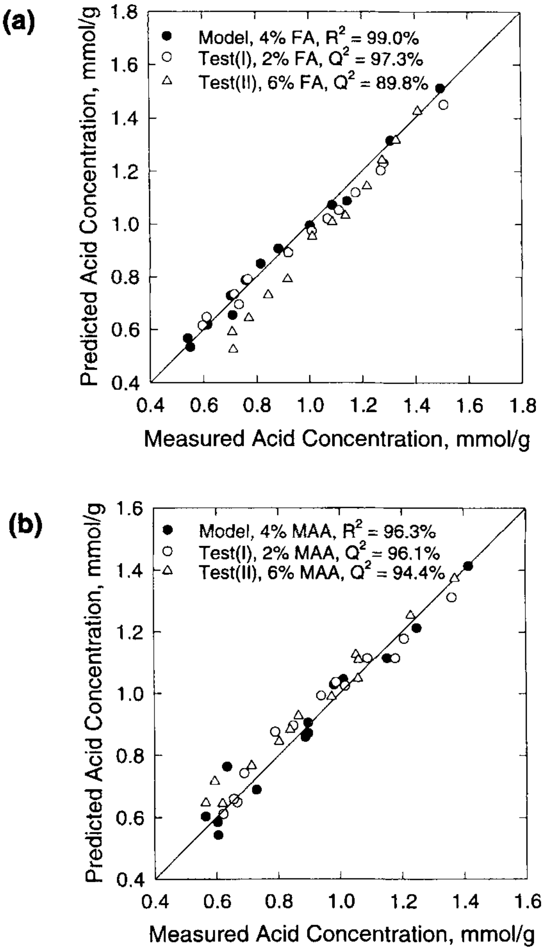


Figure 7. Measured and predicted acid concentrations in fortified Ca-resinate syntheses.

Linear PLS calibration is based on FTIR spectroscopic data. Fortification with (a) fumaric acid, and (b) maleic acid anhydride.

The rosin acid fortification was observed to affect the value of the decarboxylation reaction order of the free rosin acids. The mechanistic study therefore showed that the resinate molecules are partly solvated by the rosin acids, and that the fortified acid groups are not the solvating acids. The experimental data with the estimation of reaction-rate parameters verified the assumed decarboxylation reaction mechanism based on the rosin acids solvation phenomenon.

PLS Calibration Models for Acid Concentration. Predictive calibration models based on partial least-square regression (PLS) were developed to describe the relationship between the FTIR spectra and the acid concentration of FA- and MAA-fortified Ca-resinates. The spectra were used as the descriptor variables X in the calibration. Before PLS modeling, the calibration set was centered. The test set was then centered by means of the calibration set. The application of the PLS method is discussed in more detail in the previous study, in which the method was applied to the unmodified resinate syntheses and to the viscosity calibration of fortified industrial samples (Sundqvist et al., 1999a).

The acid concentration was calibrated with the linear PLS model. The optimal numbers of latent variables for different calibrations (Table 3) were found by cross validation (Martens and Naes, 1993).

Figures 7 and 8 show the experimental and predicted acid values for the calibration and test sets. In Figure 7 the model set was the synthesis using 4.0 wt. % fortifying substance, and in the test sets the syntheses were with 2.0 wt. % and 6.0 wt. % additions. The model set was defined to make the model universal in this fortification range. The calibration succeeded well in the 2.0 wt. % FA modification and in MAA modifications. In the synthesis using the 6.0 wt. % addition of fumaric acid, the anhydride concentration was greater (Figure 4) than in the other syntheses. That could be the reason for the lack of fit of the calibration model.

In the calibration with randomized models (Figure 8), the calibrations were made separately for the FA and MAA fortified syntheses. Every third observation was randomly included in the test set and the other observations in the calibration set. The calibration succeeded well, which is observed from the determining coefficient values for the modeling set (R^2) and for the test set (Q^2) shown in Figure 8. The randomized calibration models were found to be better than using only one of the syntheses for calibration. Furthermore, the randomized models are applicable for monitoring the resinate syntheses with different fortification degrees using 2-6 wt. % of FA or MAA. These are the typical fortification degrees of Ca-resinates to be used in the printing ink industry.

Syntheses with addition of rosin oil

In traditional fusion syntheses of Ca-resinates it is difficult to control the solution viscosity increase and to obtain a product in the target viscosity region because of the nonlinear solution viscosity increase during the decarboxylation reaction (Sundqvist et al., 1998). In the present study, rosin oil is added in order to obtain increased conversion of $Ca(OH)_2$ to resinate at 235°C and an increased degree of neutralization of rosin acids. In this way the target viscosity level (> 50 mPa·s) for the resinate can be obtained without the decarboxylation reaction. Because rosin oil formation is avoided, the mass yield of the synthesis can be increased to a higher level (almost to 100%) than in traditional fusion synthesis (about 70%), by evaporating and recycling the added rosin oil.

Derivation of an empirical correlation between the reaction mixture composition and the solution viscosity is done in

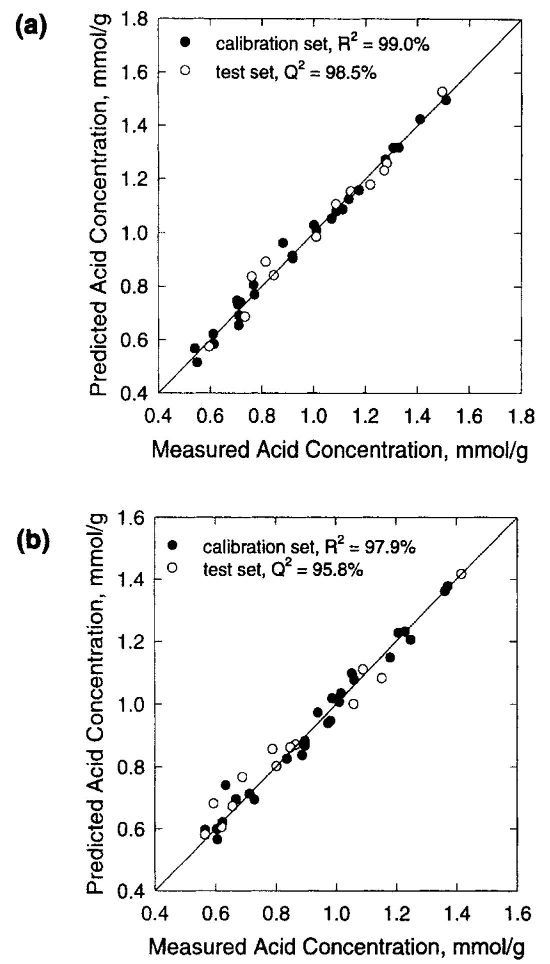


Figure 8. Measured and predicted acid concentrations in fortified Ca-resinate syntheses.

Linear PLS calibration is based on FTIR spectroscopic data. The calibration and test sets are randomly selected from the data set. Fortification with 2, 4 and 6 wt. % of (a) fumaric acid, and (b) maleic acid anhydride.

order to calculate the theoretical viscosity values for the resinate synthesized by the addition of rosin oil. The evaporation of rosin oil was studied in a thermobalance (Sundqvist et al., 2000), and therefore the viscosity of the resinate sample was not measured after evaporation in the present study. Viscosity was calculated based on an empirical correlation between solution viscosity and the reaction mixture composition. The ratio of resinate concentration to the acid concentration was used to describe the composition of the relatively complex reaction mixture.

Effect of Rosin Oil Addition/Evaporation on Resinate Viscosity. It has been observed that the solution viscosity of resinates is highly dependent on the mass concentration of the resinate in toluene (Sundqvist et al., 1998). A similar effect is observed when rosin oil is used as a solvent for the resinate (Figure 9). It is therefore necessary to evaporate all the added rosin oil from the reaction mixture, in order to obtain the target viscosity for the product.

Effect of Rosin Oil Addition on Solvation. Rosin oil was used in the syntheses as a solvent for resinate. Thus, the effect of the added rosin oil on the solvation of resinate

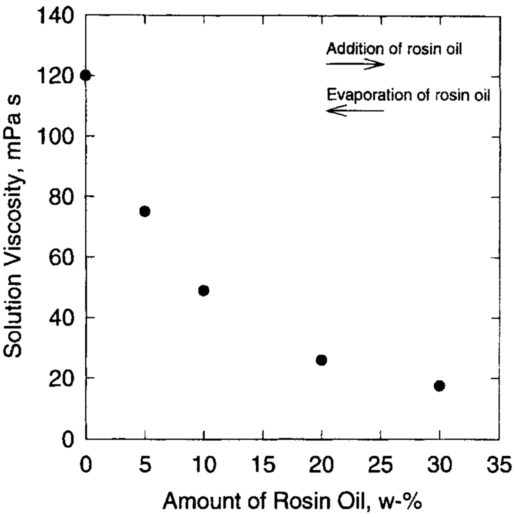


Figure 9. Effect of rosin oil addition on solution viscosity.

molecules was studied with different amounts of rosin oil added in the syntheses (Figure 10). At low degrees of neutralization [target acid values 70 and 90 mg(KOH)/g], the concentration ratio of free rosin acids to resinate increases with the increased rosin oil additions. This dilution effect is not so evident with the target acid values 0, 25, and 50 mg(KOH)/g, where the degree of neutralization is high.

Effect of Rosin Oil Addition on Conversion. The high degree of neutralization of rosin acids is required in order to obtain the target viscosity for the resinate. In traditional fusion syntheses, the decarboxylation of rosin acids forming neutral rosin oil results in a high degree of neutralization. In the modified syntheses with rosin oil additions, the rosin acids can be highly neutralized through the increased conversion of $Ca(OH)_2$ to resinate. Figure 11 indicates that the conversion of $Ca(OH)_2$ to resinate depends on the theoretical target acid value (degree of neutralization). Using target acid values 0 and 25 mg(KOH)/g, the conversion is significantly increased by the addition of rosin oil. When the degree of neutralization is smaller [with target acid values 50, 70, and 90 mg(KOH)/g], the conversion is about 90% without adding rosin oil, and the effect of rosin oil on the conversion is not so clear.

Calculation of Theoretical Viscosity Values for the Product. A solution viscosity of 50 wt. % resinate–toluene solution is an important quality factor for resinates to be used as an ink vehicle. An empirical correlation between the viscosity and acid concentration was introduced in our earlier study (Sundqvist et al., 1998). However, in order to specify the empirical correlation between the viscosity and the chemical composition of the reaction mixture, the composition is described with the ratio of resinate concentration to the acid concentration (Figure 12), and the empirical correlation, Eq. 10, is thus obtained:

$$\frac{1}{\eta} = 0.02105\left(\frac{c_{\mathrm{resi}}}{c_{\mathrm{acid}}}\right)^2 - 0.10568\left(\frac{c_{\mathrm{resi}}}{c_{\mathrm{acid}}}\right) + 0.13490. \quad (10)$$

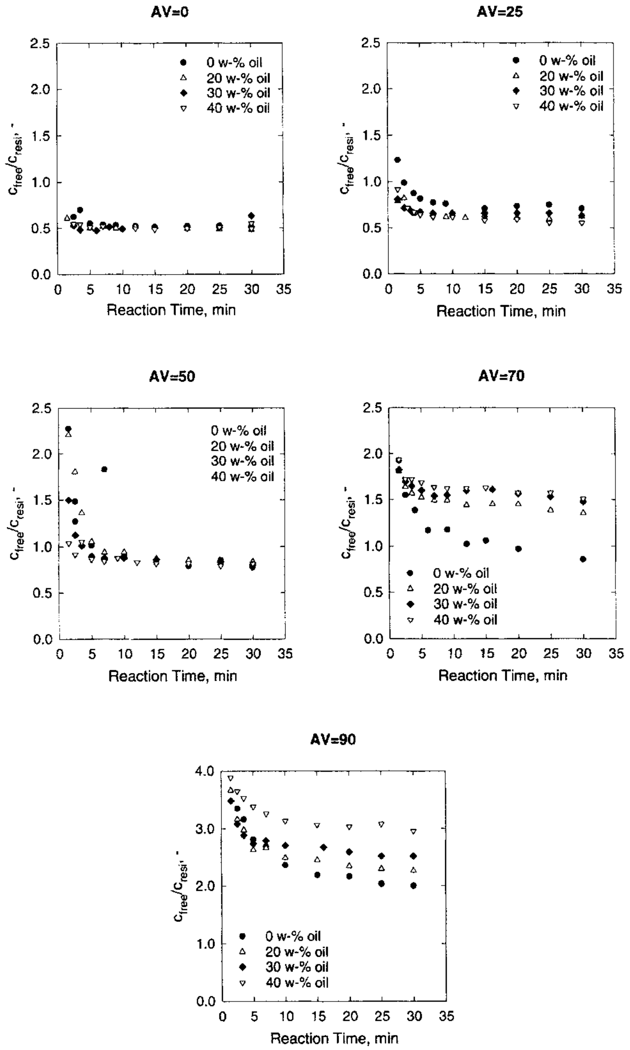


Figure 10. Ratio of free rosin acid concentration to resinate concentration with different theoretical target acid values (AV) used in the syntheses.

Rosin oil additions are 0–40 wt. %.

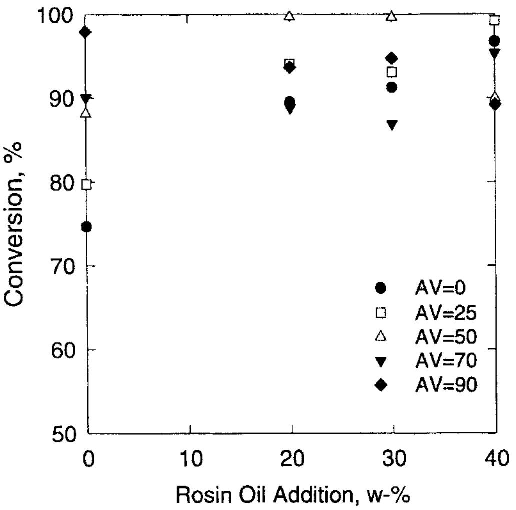


Figure 11. Effect of rosin oil addition on the conversions of $Ca(OH)_2$ to resinate in the fusion syntheses with different theoretical target acid values (AV).

The theoretical viscosity values (Table 4) were calculated for the 50 wt. % resinate–toluene solution according to Eq. 10. In the calculations, it was assumed that all the added rosin oil had been evaporated from the reaction mixture.

In conclusion, the resinate to be used in the printing industry can be synthesized with the target viscosity value (> 50 mPa·s) using theoretical target acid value 0 mg(KOH)/g and rosin oil additions 30 and 40 wt. %. The target viscosity then is obtained by the conversion of 90–95% $Ca(OH)_2$ to resinate.

Conclusions

This study showed that the kinetics of fortified resinate syntheses using fumaric acid (FA) and maleic acid anhydride (MAA) as fortifying substances can be described by basically the same mechanistic model as previously derived for unmodified resinate syntheses. The acid groups in the fortified rosin are observed to be free acid groups capable of associating to dimers in toluene. The free acid groups of fortified rosin are observed to decarboxylate via ion-pair formation, resulting in an apparent reaction order of 4.0 for the free acids.

In the FA or MAA-fortified resinate syntheses, multivariate calibration models using a linear PLS regression were applied to monitor the decrease in acid concentration on the basis of FTIR spectroscopic data. Randomized calibration

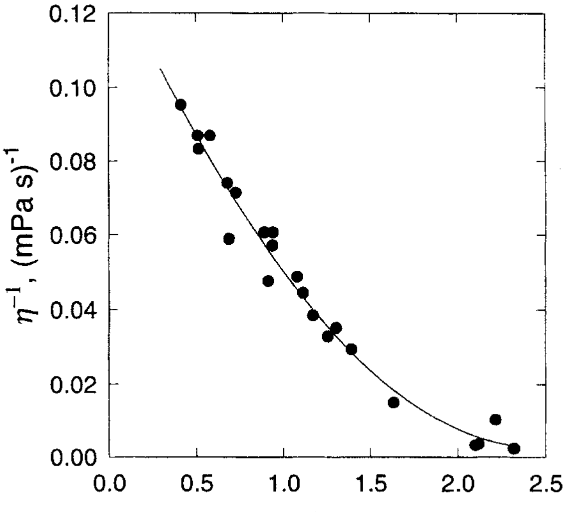


Figure 12. Empirical correlation between the viscosity of 50 wt. % resinate–toluene solution and the composition of the reaction mixture described as the concentration ratio of resinate to rosin acids.

The curve is calculated according to Eq. 10.

Table 4. Composition of the Resinate with Rosin Oil Addition*

Target Acid Value mg(KOH)/g	Rosin Oil Addition wt. %	Rosin Acid Conc. mmol/g	Resinate Conc. mmol/g	$c_{\mathrm{resi}}/c_{\mathrm{acid}}$	Calc. Visc. mPa·s
0	0	0.692	1.077	1.56	45.6
	20	0.660	1.008	1.53	43.4
	30	0.583	0.980	1.68	55.7
	40	0.476	0.982	2.06	122
25	0	0.925	1.005	1.09	23.1
	20	0.840	0.910	1.08	23.0
	30	0.797	0.855	1.07	22.7
	40	0.675	0.855	1.27	29.7
50	0	1.042	0.905	0.87	17.2
	20	1.002	0.823	0.82	16.2
	30	0.950	0.785	0.83	16.3
	40	1.023	0.635	0.62	12.6
70	0	1.327	0.765	0.58	12.0
	20	1.396	0.626	0.45	11.0
	30	1.377	0.539	0.39	11.1
	40	1.368	0.578	0.42	11.0
90	0	1.410	0.650	0.46	11.0
	20	1.537	0.514	0.33	—
	30	1.554	0.494	0.32	—
	40	1.886	0.460	0.24	—

*The viscosity values of 50 wt. % resinate–toluene solutions are calculated according to Eq. 10, assuming that all the added rosin oil has been evaporated.

data, using different amounts of fortifying substances in the syntheses (2–6 wt. %), gave useful models to be applied for process monitoring within the range of degrees of fortification studied.

In addition, in this study a new modification of resinate synthesis, which includes the addition of rosin oil during the fusion synthesis, was introduced. The modified syntheses were carried out at a lower reaction temperature (235°C) than tradition fusion synthesis (265°C). The decarboxylation reaction was therefore avoided during the syntheses. Using a stoichiometric amount of $Ca(OH)_2$ to neutralize all the rosin acids, the conversion of $Ca(OH)_2$ to resinate increased from 75% to 95%, when the rosin oil was added during the resination reaction step. The target viscosity of the resinates is then obtained by evaporation of the added rosin oil. Recycling the rosin oil enables the mass yield to be increased from 70% to almost 100%.

Notation

c_i = concentration of compound i, mol/kg
c_1 = resinate concentration at time t_1, mol/kg
c_2 = resinate concentration at time t_2, mol/kg
$c_{\mathrm{RCOOH(s)}}$ = concentration of solvating rosin acids, mol/kg
$c_{\mathrm{RCOOH(f)}}$ = concentration of free rosin acids, mol/kg
c_x = concentration of ion pairs (Eq. 4), mol/kg
k'' = rate constant for the decarboxylation reaction, $(\mathrm{mol/kg})^{1-\alpha}\cdot\mathrm{min}^{-1}$
k_1 = rate constant for the decarboxylation of solvating rosin acids, $(\mathrm{mol/kg})\cdot\mathrm{min}^{-1}$
k_2 = rate constant for the decarboxylation of free rosin acids, $(\mathrm{mol/kg})^{-3}\cdot\mathrm{min}^{-1}$
K_{ass} = equilibrium constant for the protolysis of free rosin acids
K'_{ass} = equilibrium constant for the protolysis of fortified rosin acids
m_1 = mass of the reaction mixture at time t_1, kg
m_2 = mass of the reaction mixture at time t_2, kg
n_i = amount of i in the reactor, mol
r_i = generation rate of compound i, $(\mathrm{mol/kg})^{1-\alpha}\cdot\mathrm{min}^{-1}$

Greek letters

α = reaction order
Δm_{rel} = relative mass loss

Abbreviations

AV = acid value
FA = fumaric acid
MAA = maleic acid anhydride
PLS = partial least-square regression
R^- = carbanion intermediate

Literature Cited

Haario, H., *MODEST-User's Guide*, Profmath, Helsinki (1994).

Hindmarsh, A. C., "ODEPAK—A Systematized Collection of ODE-Solvers," *Scientific Computing*, R. Stepleman, et al. (eds)., IMACS/North-Holland, Amsterdam (1983).

Jilek, J., "Calcium Salts of Tall Oil Rosin," *J. Coating Technol.*, **48**, 83 (1976).

Martens, H., and T. Naes, *Multivariate Calibration*, Wiley, Chichester, UK (1993).

Oldring, P., and G. Hayward (eds.), *Resins for Surface Coatings*, Vol. 1, SITA Technology, London (1987).

Petrone, J. P., "Synthetic Resins for Inks I: Limed and Zinc Resinates, Rosin Esters," *Amer. Ink Maker*, **49**, 27 (1971).

Spendley, W., G. R. Hext, and F. R. Humsworth, "Sequential Application of Simplex Design in Optimization and Evolutionary Operation," *Technometrics*, **4**, 441 (1962).

Sundqvist, S., E. Paatero, A. Klemola, and H. Tenhola, "Solution Viscosity Increase in Fusion Synthesis of Ca/Mg-Resinates," *AIChE J.*, **44**, 1680 (1998).

Sundqvist, S., M. Leppämäki, E. Paatero, and P. Minkkinen, "Application of IR Spectroscopy and Multivariate Calibration to Monitor the Fusion Synthesis of Ca- and Ca/Mg-Resinates," *Anal. Chim. Acta*, **391**, 269 (1999a).

Sundqvist, S., E. Paatero, and H. Tenhola, "Resination and Decarboxylation Reactions in Fusion Synthesis of Ca-Resinates," *Can. J. Chem. Eng.*, **77**, 465 (1999b).

Sundqvist, S., S. Turunen, and E. Paatero, "Decarboxylation of Rosin Acids in Fusion Synthesis of Ca-Resinates—Thermogravimetric Studies," *Can. J. Chem. Eng.*, **78**, 928 (2000).

Sykes, P., *A Guidebook to Mechanism in Organic Chemistry*, 6th ed., Wiley, New York (1986).

Zinkel, D. F., and J. Russel (eds.), *Naval Stores*, Pulp Chemicals Association, New York (1989).

Manuscript received Nov. 2, 1999, and revision received May 22, 2000.