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Phase miscibility in oil/resin mixtures: a study by FTIR and thermomechanical analysis

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Abstract

Quantitative infrared analysis in the carbonyl region with a simple curve-fitting procedure and thermomechanical measurements were used to analyse critical behaviours in naturally aged oil/resin mixtures covering a wide range of composition. The results are discussed on the basis of a comparative study performed with fresh mixtures of the same composition, used as standards, and a phase miscibility analysis.

Thermomechanical measurements give macroscopic evidence for phase segregation in naturally aged mixtures with a resin component content strictly below 50%, while above this threshold the basic components are totally involved in the formation of a stable mixed oil/resin phase. At the molecular scale, infrared measurements appear to be sensitive to the subsequent oil/resin interaction in aged mixtures which appears to develop at the first stage of the mixing.

Keywords: Ageing; Oil/resin systems; Phase segregation; Quantitative infrared; Thermomechanical analysis

1. Introduction

Because they exhibit a strong thixotropic character at room temperature at the initial stage of mixing, oil/resin systems constitute attractive media for natural paints.

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Nevertheless, their use is rather constrained as large variations in the physical properties of aged mixtures are generally observed as a function of their composition.

This work provides evidence of critical behaviour in definite concentration ranges of the basic components in naturally aged mixtures. These are observed by thermomechanical (TMA) and infrared analysis (FTIR) and discussed on the basis of a comparative study with fresh mixtures of the same composition, used as references. While the TMA technique provides information at the macroscopic level on the mechanical properties of the mixtures, FTIR measurements support the study at the mesoscopic level and allow recognition of physical interactions, if any, between their basic components [1–3]. The interpretation of the FTIR data is supported by a simple curve-fitting procedure performed in the carbonyl region of the absorption spectra. Finally, a natural correlation is expected between the behaviour of the mixtures deduced from the combined TMA/FTIR analysis and the quality of their phase miscibility as observed by eye.

2. Materials and techniques

2.1. Materials

Linseed oil consists of a mixture of triglycerides with a range of saturated and unsaturated long-chain fatty acids [4] up to C_{18}. One volume of lead-oxide-based drier was added drop by drop at room temperature to 8 volumes of linseed oil in order to form the oil component. Mastic is a triterpenoid natural resin [4] (C_{30}); 10 g of mastic resin were dissolved at 80°C in 50 ml of oil of turpentine monoterpenoid (C_{10}) in order to form the resin component. A magnetic stirrer was used as the mixer. Both mixtures were stirred at low and constant speed during the adding process and again 30 min after so as to obtain clear, homogeneous substances.

Five oil/resin systems were prepared with the oil and resin components described above as starting materials. They correspond to volume proportions of the resin components of 25%, 33.3%, 50%, 66.6% and 75%, and are respectively labelled as mixtures 1–5. The procedure consisted of placing the appropriate volume of the oil component in the mixer and adding the resin component drop by drop with the stirrer set at low speed. Once the full amount of the resin component had been added, the mixture was stirred for 10 min at low speed to ensure homogeneity, and then transferred to a quart bottle and capped to prevent evaporation. A piece of ordinary aluminium foil was used as a liner for the screw caps of the quart bottle. All mixtures have a gel consistency at room temperature. After their preparation, all the mixtures appear as homogeneous gels.

Some of the measurements were performed with naturally aged materials. After their preparation, these were deposited as thin films on glass substrates and left in the open air at room temperature and in the dark for 5 months.

Labels 1–5 are relative to the composition of the mixtures and design, independent of fresh and naturally aged materials. Volumes and weight were respectively accurate to 0.2 ml and 0.01 mg.

2.2. Techniques

Differential scanning calorimetry (DSC) measurements were performed with a constant heating rate using a Seiko 220C instrument: the heat flow between the sample and the reference, placed in open crucibles within a Boersma-like calorimeter, is recorded as a function of the temperature with the endothermic (positive) position downward. N_2 was used as a purge gas. The principles of the analysis of the DSC measurements are described more extensively elsewhere [5, 6].

FTIR spectra were acquired from 4000 to 650 cm^{-1} at 4 cm^{-1} resolution using a TGS detector, and averaged over 30 scans. They were run unpurged and the data collection time was 2 min. Two different methods were used to perform infrared measurements according to the nature of the mixtures. The details of the principles [7] and techniques [8] are described more extensively elsewhere.

As fresh materials present contact properties similar to those of a liquid, their infrared spectra were collected with the attenuated total reflectance (ATR) technique. The absorption volume is fixed by the refractive index which has the same value for the oil and resin components, namely 1.5. In these conditions the same absorption volume is investigated in all the mixtures which allows the direct comparison of their infrared signal. ATR spectra were analysed by a Micolet 510 spectrometer; the crystal fitted to the ATR equipment was a 12-reflection ZnSe 45°.

Because of high surface roughness which prevents good quality contact at the ZnSe–sample interface, satisfactory ATR spectra from naturally aged mixtures could not be obtained. An arbitrary amount of each sample was removed from the glass substrate, placed on a KBr disc, and heated at 60°C so as to soften the material and remove the voids in the bulk. The latter resulted from the evaporation of the oil of turpentine and led to a parasite diffusion of the infrared light which greatly affected the quality of the spectra. The heating process lasted 30 s, after which a second KBr disc was placed over the sample and pressed on the first. The whole structure was then removed from the oven and analysed by transmission. As the thickness of the sample is not monitored, a direct comparison of the infrared spectra was not possible. Infrared spectra recorded in transmission with the oil and resin components using the same definite pathlength were used as references for the analysis of the above mixtures.

Thermomechanical measurements were performed in penetration mode, under the controlled force procedure, with a Perkin-Elmer 7 series thermal analysis system, using a cylindrical probe, 1 cm in length and 1 mm in diameter. TMA curves were recorded from −60°C up to 100°C at a heating rate of 2°C min^{-1}. Static forces of 1 mN and 10 mN were respectively applied to the fresh and naturally aged mixtures. For some specific samples, different static forces were applied in order to reveal clearly their softening transitions.

Fresh and naturally aged mixtures, and their basic components, were analysed in circular crucibles, 3 mm in diameter and 1 mm in height, so as to define a fixed geometry for all the measurements. Fresh mixtures and the basic components were poured directly in the crucibles. In order to investigate the bulk rather than the surface properties of naturally aged mixtures, large pieces of the thin films were removed from the glass substrates, deposited in the crucibles, and heated at 60°C for 30 s, so as to define a thick, homogeneous sample.

As the thickness of the samples was not monitored, a direct comparison of the TMA curves was not possible; attention is then mainly focused on the positions of the transitions.

3. Experimental results

3.1. DSC measurements

DSC analysis was used to determine the main thermodynamic transitions of the basic components. DSC curves obtained with a constant heating rate of 7°C min^{-1} in the temperature range from -150°C up to 200°C with freshly prepared mastic resin and oil component are reported in Fig. 1.

3.2. FTIR measurements

ATR spectra of the lead-based drier, the oil, the oil of turpentine and the resin component are reported in Fig. 2.

For each mixture and basic component, the shape of the infrared absorption structures in the carbonyl region has been systematically analysed in a quantitative way by a curve-fitting procedure using the same set of four Lorentzian functions. Their characteristic parameters are reported in Table 1. The positions and widths at half height were fixed; only the intensities were adjustable. ATR spectra obtained with the basic components and the fresh mixtures are respectively reported in Figs. 3 and 4 with the results of the curve-fitting procedure. For fresh materials, the evolution of the carbonyl areas associated with the oil and resin components as a function of the composition of the mixtures is reported in Fig. 5. Transmission spectra obtained with the basic components and the naturally aged mixtures are respectively reported in Figs. 6 and 7 with the results of the curve-fitting procedure. For fresh and naturally aged materials, the evolution of the ratio of the carbonyl areas related to the oil and resin components are respectively reported in Fig. 8a and 8b.

3.3. Thermomechanical measurements

The thermomechanical curves obtained with the oil component and the fresh mixtures are reported in Fig. 9. Considering mixture 4, additional measurements were performed under the same experimental conditions but with greater applied forces, namely 10 and 50 mN. These are reported in Fig. 10. The thermomechanical curves obtained with the naturally aged mixtures are reported in Fig. 11. From calibration with pure distilled water, it appears that a typical experimental error of ±2°C is to be expected for the precision in the determination of the softening transitions.

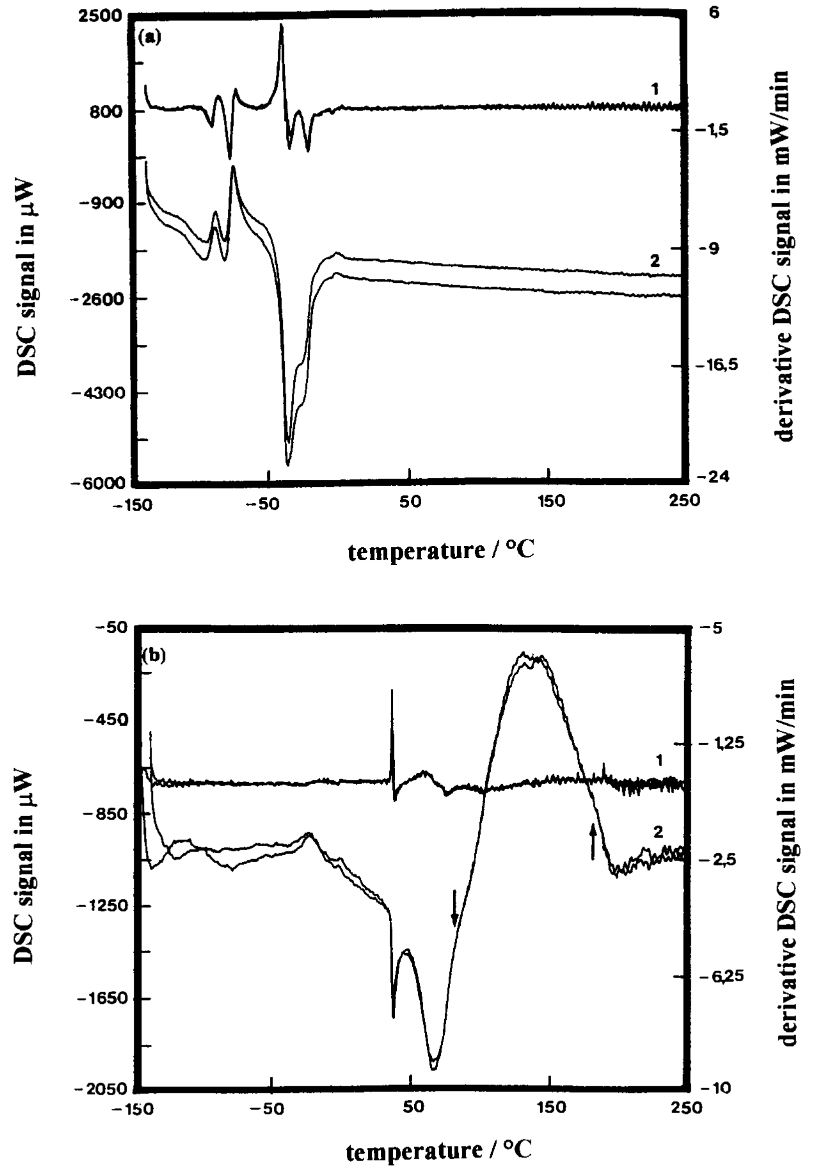

Fig. 1. DSC curves obtained with a constant heating rate of 7°C $\min^{-1}$ in the temperature range −150°C to 250°C with the oil component freshly prepared (a) and pure mastic resin (b). In each case, the measurements were performed under the same experimental conditions with two different samples from the same material. Labels 1 and 2 refer respectively to the DSC curve and its first derivative.

4. Discussion

The DSC measurements are presented first; they were used as a basis from which to define the thermal context of the combined FTIR/TMA analysis.

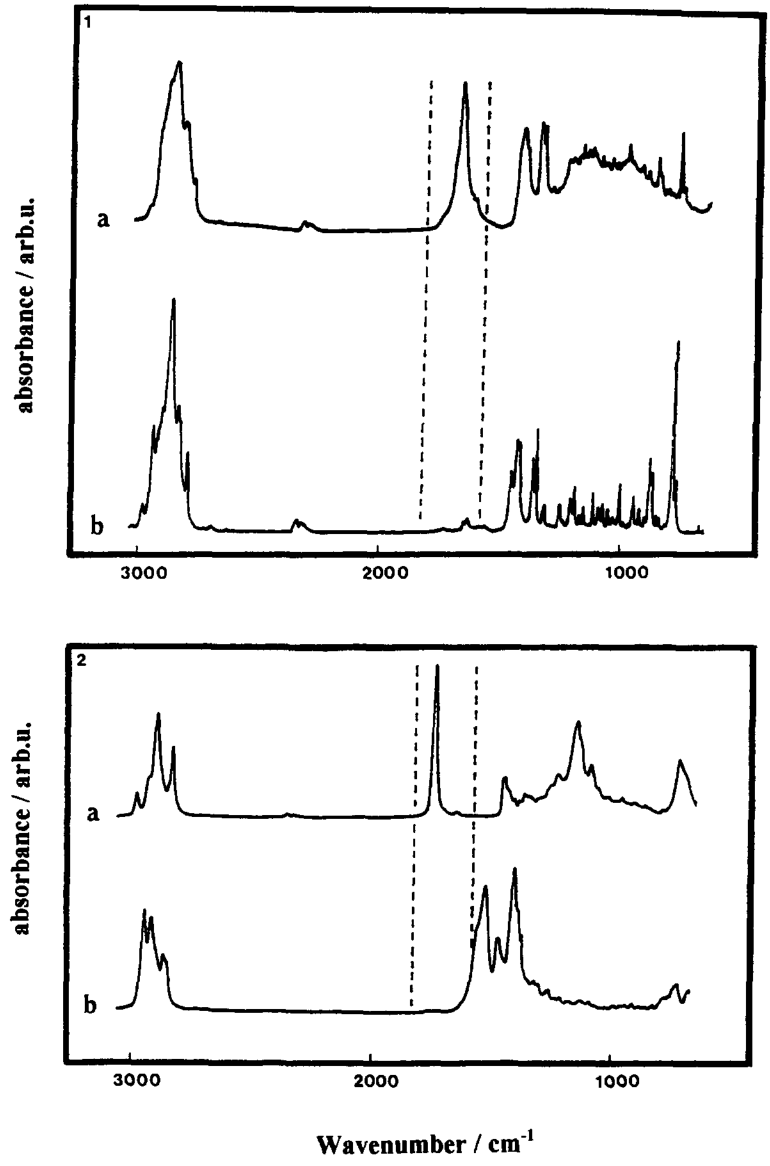

Fig. 2. ATR infrared spectra obtained with the basic constituents of the resin (1) and the oil (2) components: the resin component (1a); the oil of turpentine (1b); the oil (2a) and the drier (2b). The carbonyl region, where the curve-fitting procedure is applied, is delimited by dashed lines.

4.1. DSC measurements

DSC curves obtained with the oil and resin components show two exothermic transitions, at −87°C and −75°C, and two endothermic transitions, at −33°C and

Table 1
Characteristic fixed parameters of the four Lorentzian functions used for the curve-fitting procedure

Lorentzian peaks	Position/cm^{-1}	Half width at full height/cm^{-1}
1	1769	20
2	1742	15
3	1720	20
4	1703	15

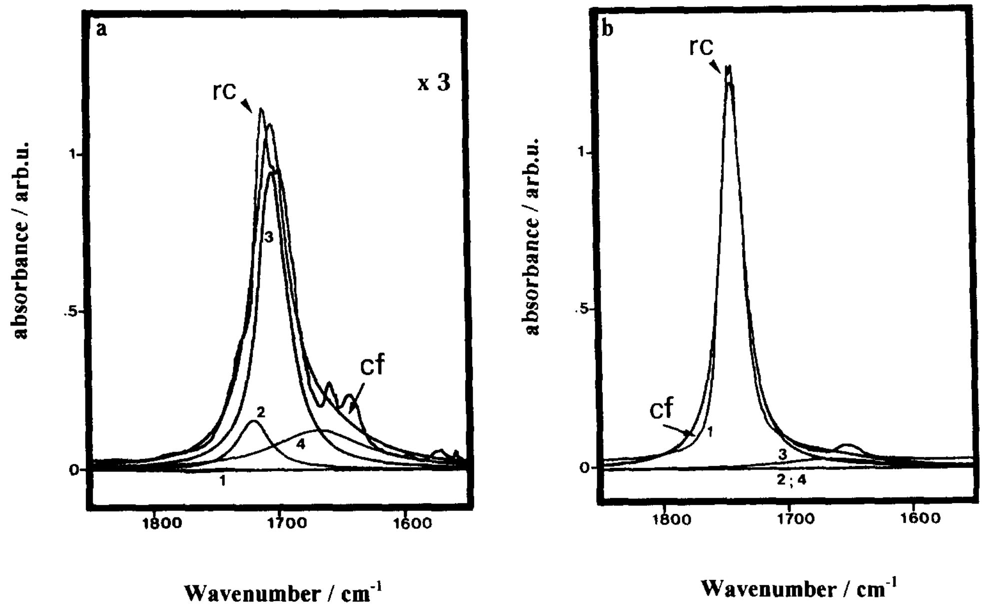

Fig. 3. ATR infrared spectra obtained with the resin (a) and the oil (b) components. Labels 'rc' refer to the experimental curves. The Lorentzian structures used for the curve-fitting procedure are reported together with the resulting fitting curve, labelled 'cf' for each material. Numbers 1 to 4 refer to the corresponding Lorentzian functions in Table 1.

−25°C. The first two processes are interpreted as partial crystallization processes generated respectively by segmental and chain motions. When increasing the temperature, it is proposed that thermally activated molecular motions take place on the same scale and destroy the macroscopic order. DSC structures located at −33°C and −25°C are thus interpreted as partial melting transitions.

As it is prepared with a high proportion of oil of turpentine, which is highly volatile, it is extremely difficult to perform successful DSC measurements with the resin component. Consequently, basic information concerning thermodynamic transitions in the resin component were extracted from DSC measurements performed with pure mastic resin. DSC curves obtained with the latter material exhibit two exothermic transitions,

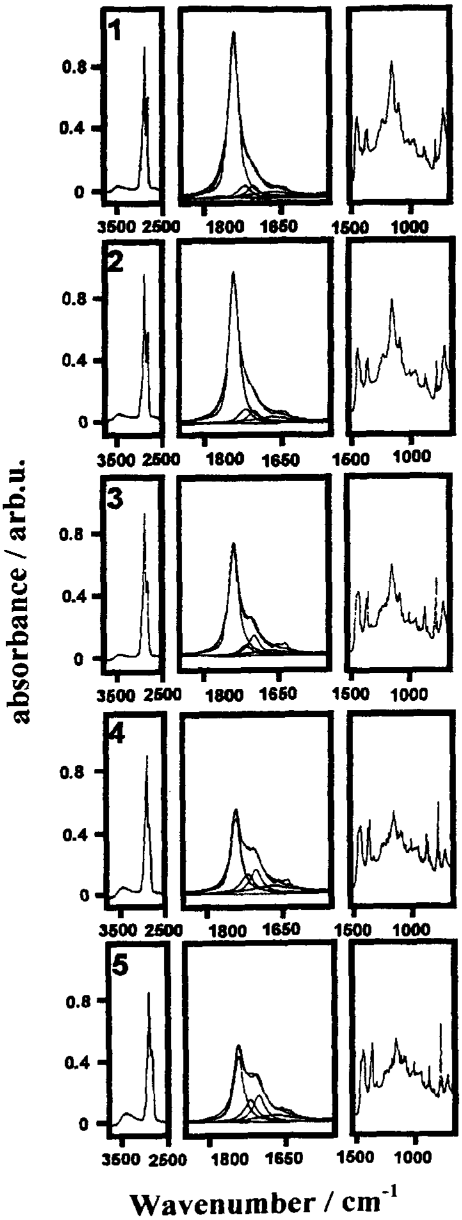

Fig. 4. ATR infrared spectra performed with fresh mixtures. Labels 1 to 5 refer to the corresponding compositions of the mixtures. The Lorentzian structures used for the curve-fitting procedure are reported together with the resulting fitting curve for each material.

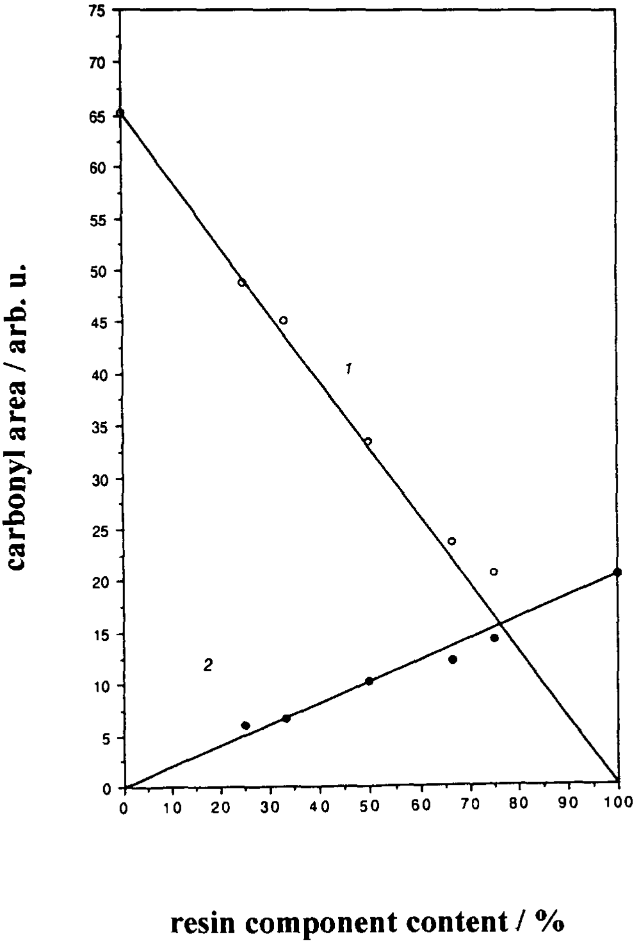

Fig. 5. Infrared carbonyl areas deduced for the oil and resin components from the curve-fitting procedure performed with fresh mixtures. Straight lines 1 and 2 represent the ideal expected areas in the mixtures when considering a linear relation between the magnitude of the carbonyl areas associated respectively with the oil and resin components alone (refer to Fig. 3) and their amount in the mixtures. solid and open circles refer to experimental data.

at −25°C and 140°C, and two endothermic transitions, at 32°C and 70°C. In addition thermomicroscopy observations performed with mastic resin from room temperature up to 200°C at a constant heating rate of 7°C min^{-1} show that mastic resin changes from a powder to a liquid when going through the transition at 70°C, and undergoes an irreversible alteration in colour from clear yellow to dark brown at 140°C. Transitions observed at 70 and 140°C are thus respectively attributed to the melting [9] and the denaturation of mastic resin. The two structures which appear at lower temperatures are not assigned.

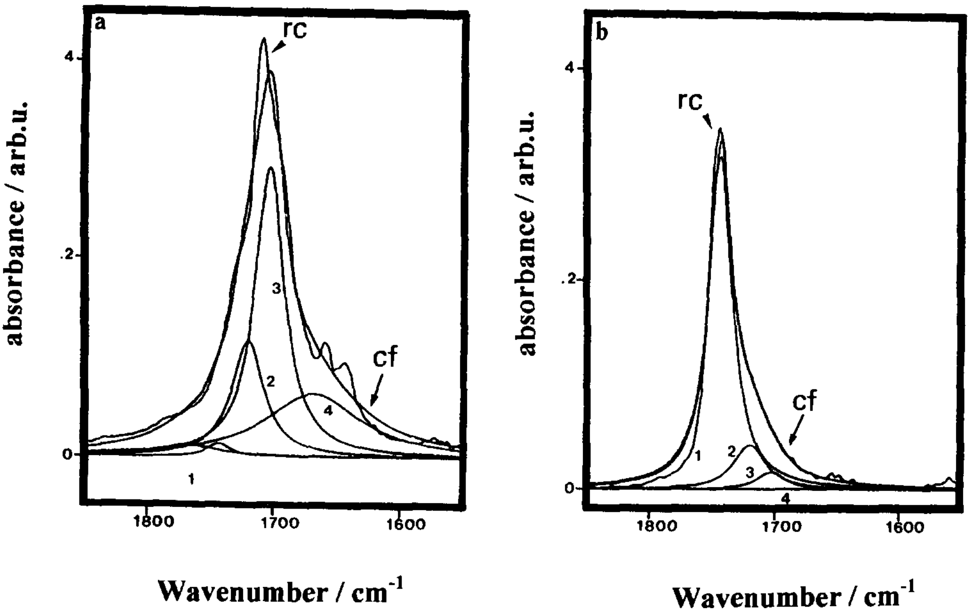

Fig. 6. Infrared spectra recorded in transmission with the resin (a) and the oil (b) components. They were recorded with the same definite pathlength of 0.9015 mm. Labels 'rc' refer to the experimental curves. The Lorentzian structures used for the curve-fitting procedure are reported together with the resulting fitting curve, labelled 'cf' for each material. Numbers 1 to 4 refer to the corresponding Lorentzian functions in Table 1.

4.2. Infrared measurements

4.2.1. Basic materials

Pure mastic resin appears as a dense powder at room temperature and parasite diffusion due to voids in the structure greatly affects the quality of the ATR spectra. In these conditions, basic information concerning the infrared responses of the constituent materials of the resin component were obtained from the comparison of the ATR signals delivered by the resin component itself and the oil of turpentine. In the carbonyl region, which spreads from 1550 cm^{-1} to 1850 cm^{-1}, the oil of turpentine has a negligible contribution to the infrared signal in comparison with the intense structure located at 1702 cm^{-1}, attributed by difference to pure mastic resin. Concerning the oil component, the lead-based drier has no contribution to the infrared signal in the carbonyl region, while the structure at 1742 cm^{-1} constitutes a clear indicator for the oil. The carbonyl region thus appears to be the zone of choice to investigate the oil/resin relation without considering, to a first approximation, the separate influences of the lead-based drier and the oil turpentine. The latter will be discussed below.

To this end, a curve-fitting procedure has been developed in the carbonyl region. A suitable set of Lorentzian function [10] has been chosen so that after the curve-fitting the reconstructed oil-like contribution to the total absorption area of the resin component does not exceed 5%, and vice versa. Using this procedure, with a small

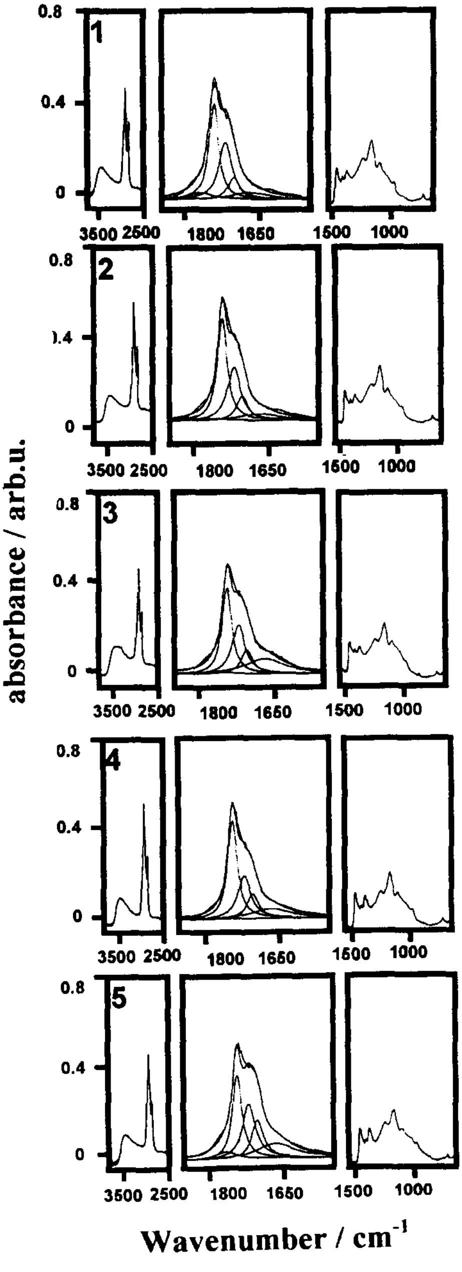

Fig. 7. Infrared spectra recorded in transmission without a definite pathlength with naturally aged mixtures. The Lorentzian structures used for the curve-fitting procedure are reported together with the resulting fitting curve for each material. Number 1 to 5 refer to the corresponding mixtures.

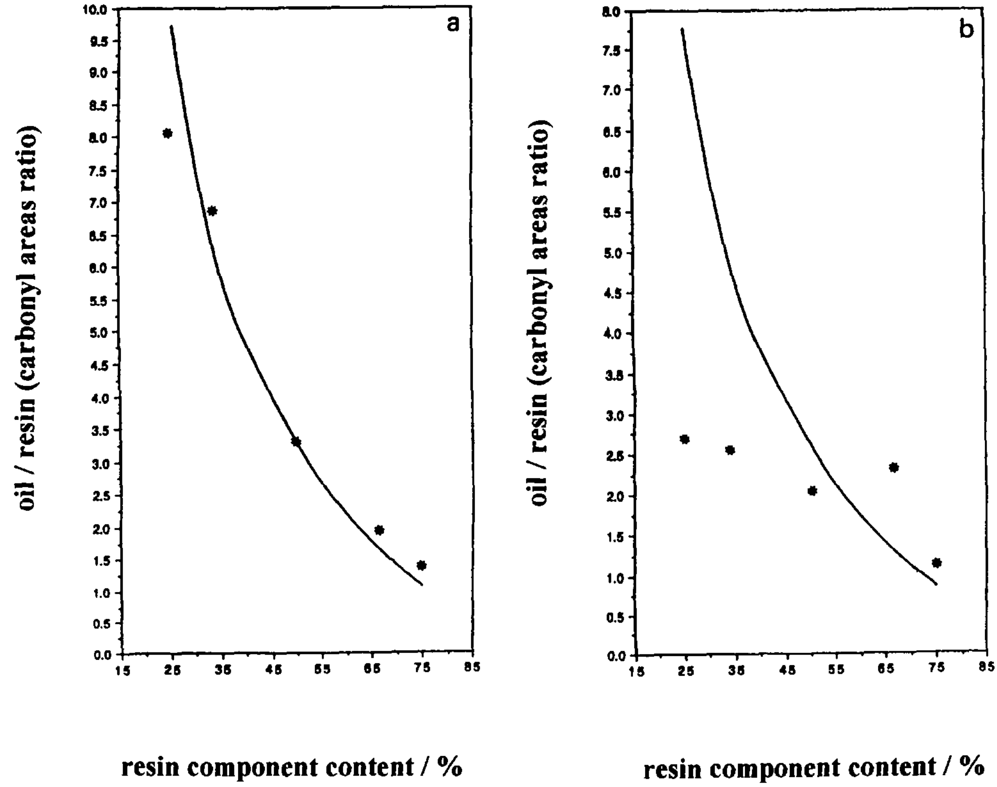

Fig. 8. Evolution of the ratio of the carbonyl areas related to the oil and resin components deduced from the curve-fitting procedure, as a function of the composition of fresh (a) and naturally aged (b) mixtures. Plain lines correspond to the ideal curves expected when considering a linear relation between the magnitude of the carbonyl areas associated with the basic components (refer to Fig. 3 and Fig. 6). Black dots correspond to experimental data.

number of adjustable parameters, allows one (i) to fit satisfactorily the experimental infrared spectra obtained with the oil and resin components; and (ii) to extract their individual contributions to the total area of the absorption peaks obtained with the mixtures. Considering point (i), two different sets of intensities were considered for the Lorentzian functions, as measurements were performed differently with the ATR and transmission techiques. Considering point (ii), the individual contributions of the oil and resin components to the carbonyl signal of the considered mixture were reconstructed from the calibration described above which resulted in a curve-fitting of the carbonyl region with two ajdustable parameters. In each case, the difference between the theoretical and the experimental carbonyl areas did not exceed 10%.

4.2.2. *Fresh mixtures*

The ATR technique allows a direct quantitative comparison of the carbonyl areas from one mixture to the other because absorption volumes are identical for all the

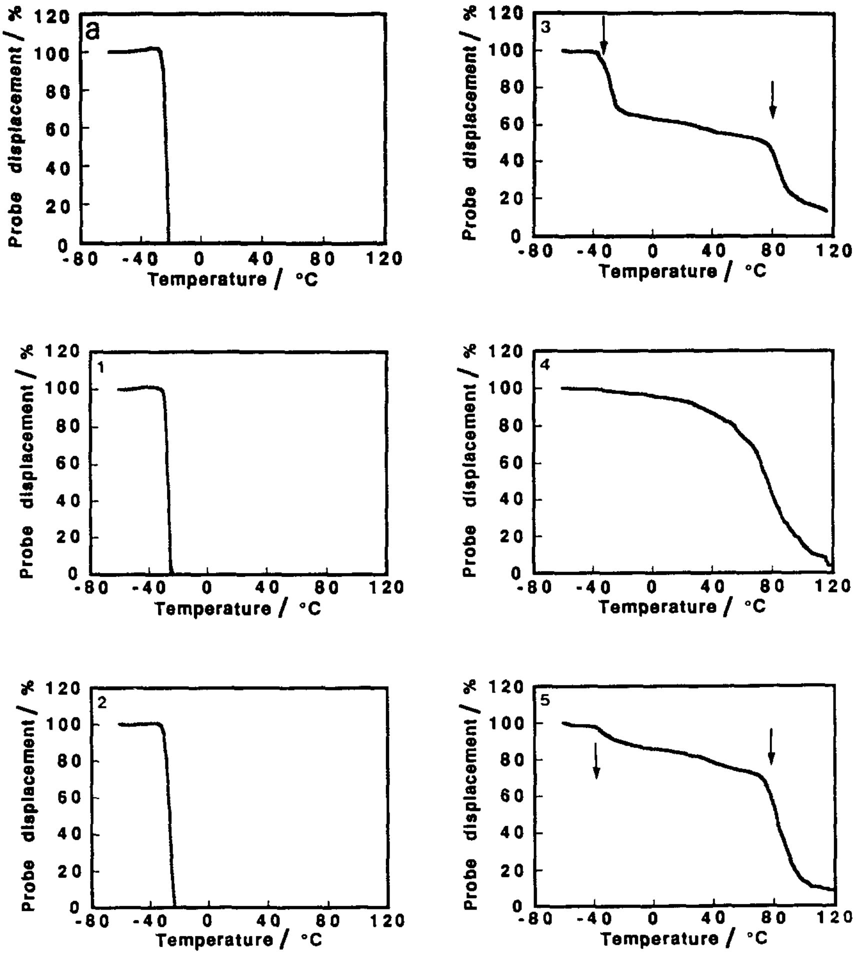

Fig. 9. Thermomechanical curves obtained with the oil component (a) and fresh mixtures with a static force of 1 mN. Labels 1 to 5 refer to the corresponding compositions of the mixtures.

materials over the whole range of composition. In this case, distinct evolution of the carbonyl areas associated with the oil and resin components can be considered as functions of the composition of the mixtures. Quasi-linear evolutions are obtained; determined ideally by the experimental points related to the oil and resin components. The divergence between the experimental points and the ideal curves when approaching small total carbonyl areas is attributed to the simple nature of the curve-fitting procedure.

The infrared responses of the oil and resin components in fresh mixtures correspond ideally to the individual responses of these materials multiplied by their content in the mixtures.

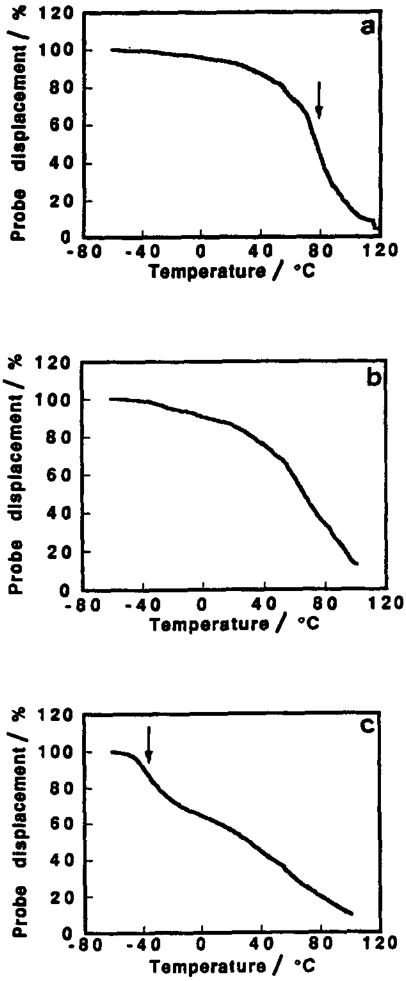

Fig. 10. Thermomechanical curves obtained with mixture 4 with different static forces of 1 mN (a), 10 mN (b) and 50 mN (c).

4.2.3. Naturally aged mixtures

Infrared spectra of naturally aged materials were recorded in transmission and the absorption volumes were not monitored. In order to eliminate this unknown parameter, the analysis was concerned with the evolution of the ratio between the carbonyl areas of the oil and resin components as a function of the composition of the mixtures. The similar evolution obtained with the fresh mixtures is also considered. Each of these was compared with the ideal curve obtained from the sole consideration of the infrared spectra of the basic components recorded with the same absorption volume but different techniques (ATR or transmission when considering respectively the fresh and aged materials).

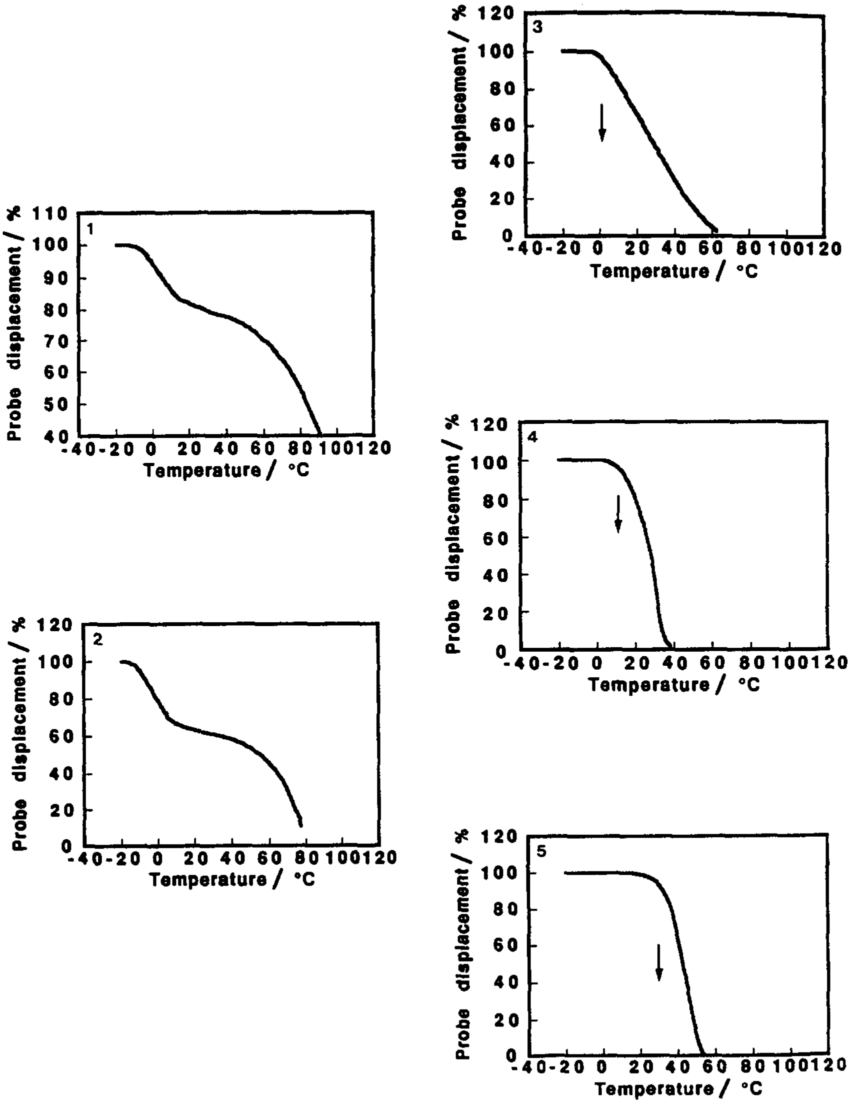

Fig. 11. Thermomechanical curves obtained with naturally aged mixtures with a static force of 10 mN. Lables 1 to 5 refer to the corresponding compositions of the mixtures.

While for fresh mixtures the experimental points agree with the ideal curve, a clear discordance is observed for naturally aged materials. This discordance is characterized by three points: (i) strictly below a resin component of 50%, the ideal curve constitutes a large over-estimation of the experimental points; (ii) from a resin component content of 50%, the trend is reversed; (iii) there is an exception singularity for the resin component content of 66%.

Two different phenomena accompany the ageing process of the oil/resin mixtures. Firstly, the polymerization of the oil component, enhanced by the drier, leads to the formation of a tri-dimensional network of triglyceride units [11]. Secondly, the progressive loss of the volative constituent of the resin component, namely the oil of turpentine, increases the density of the structure of the mixtures. The latter process does not affect the carbonyl region of the infrared spectra as it merely corresponds to the disappearance of the weak structure located at 1680 cm^{-1}. However, the polymerization process induces a decrease in the intensity of the infrared signal in the carbonyl region [10]. It is therefore taken as being responsible for effect (i). When considering only the polymerization process, the above-mentioned over-estimation should be observed over the whole composition range but with decreasing amplitude as the oil component content decreases, which is in contradiction with points (ii) and (iii). The corresponding behaviours are discussed in more detail below.

4.3. Thermomechanical measurements

4.3.1. Basic materials

The thermomechanical curve of the oil component shows only one softening transition, at −25°C. Its assignment is given by the DSC measurements. Because the resin component does not freeze above −150°C, thermomechanical analysis could not be performed with this material. From the DSC measurements, a major softening transition due to the resin is expected in the neighbourhood of 70°C.

4.3.2. Fresh mixtures

The thermomechanical curves are characterized by four points the first two being related to the characteristic temperatures of the softening transtions, and the others to the relative magnitude of the corresponding probe displacement with respect to the baseline: (i) mixtures 1 and 2 show only one softening transition located 10°C below that of the oil component; (ii) two softening transitions, in the regions of −35°C and 75°C, are observed with the other mixtures (iii) the amplitude of the probe displacement associated with the low-temperature transition decreases non-linearly with the composition when going from mixture 2 to mixture 3; (iv) high applied forces of 10 and 50 mN were necessary to reveal all the softening transitions of mixture 4.

The softening transitions mentioned in point (i) are attributed to the oil component. It is suggested that the resin component acts as a plasticizer of the oil component in oil- rich mixtures, and it is therefore taken as being responsible for the low-temperature shift of 10°C. The low- and high-temperature transitions observed with mixtures 3, 4 and 5 are clear indicators of, respectively, the oil and resin components. Points (iii) and (iv) indicate respectively an unexpected increase in the density for the mixtures with a resin component content superior to 50%, and an exception for mixture 4.

While the softening transitions of the basic components remain unaffected by mixing, an effective oil/resin interaction has to be considered, whatever its nature, to explain the non-linear mechanical properties in mixtures with a resin component content above 50%, with an exception for the resin component content of 66%.

4.3.3. *Naturally aged mixtures*

The thermomechanical curves are characterized by three points: (i) applied forces as large as 10 mN were necessary to reveal all the softening transitions; (ii) mixtures 1 and 2 show two softening transitions, in the regions of −10°C and 70°C; (iii) above a resin component content of 50%, a single softening transition is observed; its characteristic temperature increases linearly as the oil component content decreases.

The progressive loss of the oil of turpentine, which occurs with ageing, increases the density of the structure and hardens the mixtures. This effect is taken as responsible for point (i). Concerning point (ii) the hypothesis of a phase segregation process prevails since the above-mentioned low- and high-temperature softening transitions correspond to those of the oil and resin component respectively. Point (iii) is indicative of the total consumption of the basic components of the mixtures in favour of the formation of a stable mixed oil/resin phase.

4.3.4. *Phase miscibility analysis*

The above conclusions are in accordance with the observation, by eye, of the phase miscibility of five-month naturally aged mixtures stored in capped quart bottles in the dark at room temperature: phase segregation is confirmed in mixtures 1 and 2, while mixtures 3–5 appear as dense, homogeneous gels.

Concerning the latter materials, it is suggested that the oil/resin interaction, whatever its nature, which insures the stability of the mixed phase, induces a distortion of the original infrared signals from the basic components (shift, asymmetry, broadening) which results at a certain stage in an apparent over-estimation of the carbonyl response of the oil component. This effect is taken as responsible for points (ii) and (iii) in Section 4.2.3.

5. Conclusion

The suitability of a conjugated FTIR/TMA procedure to determine critical behaviour in naturally aged oil/resin mixtures was discussed on the basis of both a comparative study with fresh mixtures of the same composition used as references, and a phase miscibility analysis.

On the macroscopic scale, thermomechanical measurements clearly show non-linear mechanical properties in fresh mixtures when the resin component content reaches the value of 50%. In addition, a maximum in the hardness of the sample is observed for a resin component content of 66%. These effects are attributed to the existence of an effective oil/resin interaction, whatever its nature, which develops at the first stage of mixing in materials with a resin component content above 50%. This interaction appears to result in the long-term creation of a stable mixed oil/resin phase. A phase miscibility analysis confirms these conclusions: phase segregation occurs in naturally aged mixtures with a resin component content below 50%, while the other mixtures appear as dense, homogeneous gels.

On the molecular scale, a simple quantitative infrared analysis was developed in the carbonyl region with four Lorentzian functions. While the infrared responses of both the oil and resin components are not affected by mixing in fresh materials, the above procedure appears to be sensitive to the oil/resin interaction which holds the mixed oil/resin phases: the latter induces a distortion of the infrared signals which results in an apparent over-estimation of the carbonyl response of the oil component, with a maximum for the resin component content of 66%.

The practical interest of this work is to demonstrate that natural paints made of oil/resin mixtures with a resin component content below 50% develop phase segregation with time and are thus unstable in essence.

The physical significance of the critical resin component contents of 50% and 60% will be investigated at the microscopic level in a subsequent contribution. This will be realised through the combined analysis of the dielectric properties of conductor/insulator-like oil/resin mixtures by the thermally stimulated currents technique (TSC) and low frequency dielectric spectroscopy (LFDS).

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References

[1] C.D. Eisenbach, J. Hofmann and W.J. MacKnight, Macromolecules, 27 (1994) 3162.
[2] K. Sakurai, E.P. Dougles and W.J. Macknight Macromolecules, 25 (1992) 4509.
[3] R. Tannenbaum, M. Rutkowska and A. Eisenberg, J. Polym. Sci. B, 25 (1987) 663.
[4] J.S. Mills and R. White, The Organic Chemistry of Museum Objects, Butterworths, London, 1986, Chaps 3 and 8, p. 26, 83.
[5] J.L. McNaughton and C.T. Mortimer, Differential Scanning Calorimetry, Perkin-Elmer, Order No. L-604 (reprinted from IRS, Phys. Chem. Ser. 2, Vol. 10, Butterworths), 1975.
[6] E.M. Barral and J.F. Johnson, Tech. Methods Polym. Eval., 2 (1970) 1.
[7] D. Steele, Theory of Vibrational Spectroscopy, W.B. Saunders Company, London, 1971, Chaps 1,2, 3, p. 1–62.
[8] J. Yarwood, Anal. Proc., 30 (1993) 13.
[9] D.N. Goswani, J. Oil Col. Chem. Assoc., 63 (1980) 101.
[10] R.J. Meilunas, J.G. Bentsen and A. Steinberg, Studies in Conservation, 35 (1990) 33.
[11] H. Wexler, Chem. Rev., 64 (6) (1964) 591.