

## **A STUDY OF THE MECHANICAL AND SURFACE PROPERTIES OF OIL PAINT FILMS TREATED WITH ORGANIC SOLVENTS AND WATER<sup>1</sup>**

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Mechanical and surface properties of paint films treated with organic solvents and water have been investigated using a range of thermomechanical and dielectric techniques together with Fourier transform infrared spectroscopy and scanning electron microscopy. Changes in the nature of the surface after treatment were observed. The effect of water, propan-2-ol and propanone (acetone) immersion for 24 hours, and swabbing for a few minutes, on naturally aged 12 years old samples of lead white/linseed oil and burnt sienna/linseed oil could be measured directly in terms of change in the shear modulus of the paint films together with the accompanying change in the ratio of viscous to elastic components present in each system. Generally, the solvent-treated films became harder and showed reduced viscous components, whereas the water-treated samples became softer. There was a change in the dielectric properties of the leached films which pointed to the polar nature of the leachings. FTIR diffuse reflectance spectra supported this conclusion.

### **Introduction**

Oil paint films exhibit a wide range of mechanical properties [1]. They are influenced by factors such as temperature, pigment volume concentra-

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tion, pigment type, and moisture content. In consequence the paints used by artists show a variety of mechanical stiffnesses and strengths. An example of this difference can be seen in the way in which white lead paint will tend to form a fine network of brittle cracks, whereas more medium-rich paints, such as umbers, often have fewer, more separated, ductile crack patterns. Since the 1930s it has been known in the conservation literature [2] that the action of solvents on oil paint films may remove portions of the oil media. In the 1950s this phenomenon of 'leaching' was studied by Graham [3] and Stolow [4]. They both observed that leached paints would tend to be harder and more brittle materials. When cleaning paintings by the removal of surface varnish layers, it is common practice to employ organic solvents or alkaline aqueous solutions. It might be expected that both treatment could change the physical character of oil paint films.

Stolow's data on leaching implied that, for most solvents likely to be used in cleaning, the extent of leaching occurring would be related to the rate of action of the solvent on the varnish, and the diffusion coefficient of the solvent into the paint film. Since those solvents which are the more rapid diffusers frequently act more quickly on the varnish, the conservator effectively has to choose between shorter cleaning times with fast penetration, and longer cleaning with slower penetration<sup>1</sup>. Alternatively, the conservator may opt to clean with gel or paste systems on the assumption that penetration into the paint layers will be significantly retarded.

The change that may result from any of these approaches has not yet been quantified. It is therefore important to characterize in more detail the effect of different cleaning systems on paint films, so as to arrive at an objective assessment of the amount of physical change which may be caused to the paint by cleaning.

Mechanical measurements of paint properties before and after contact with cleaning agents are required. The older techniques such as tensile testing have been applied to paint films but the difficulty is that they require large samples and yield only limited information about the rheology and temperature dependence of the material. More recent thermal analysis techniques offer the possibility of obtaining these more detailed data from

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<sup>1</sup> See the paper by Stefan Michalski 'A Physical Model of the Cleaning of Oil Paint' in Preprints of the Contributions to the Brussels Congress, 3-7 September 1990: published by the International Institute for Conservation of Historic and Artistic Works.

samples as small as 2 mm, and this paper reports, for the first time, the use of a wide range of such techniques on samples of this scale. Previous work, using only thermomechanical analysis (TMA), has already applied this technique to samples from a water-damaged painting [5].

Concern with the bulk mechanical properties needs to be supplemented with study of the surface of treated paint films. Evidently, the upper layer of the paint films is both the most vulnerable because it will receive the longest contact with cleaning agents, and the most important since it is the surface that is seen. This surface and its cross-sectional structure can conveniently be examined with the use of scanning electron microscopy before and after treatment.

The aim of this paper is to assemble data obtained from thermomechanical analysis (TMA), dynamic mechanical analysis (DMA), dielectric thermal analysis (DETA), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and scanning electron microscopy (SEM), for the purpose of beginning to quantify the influence of cleaning materials upon the mechanical and physical properties of paints.

### **The paint samples**

Naturally aged paint samples were used for all the experiments. The samples were prepared in 1978 from commercial linseed oil paints by Grumbacher. A 'soft', medium-rich, burnt sienna and a 'hard', medium-lean, lead white were selected as examples of the two ends of the spectrum of paint mechanical properties. The samples had been cast in films onto Melinex and were of the order of 250  $\mu\text{m}$  thick.

#### *Treatment of the samples*

The samples were treated with water, propan-2-ol, and propanone. The water was 'Analar' quality. Samples were treated in two days:

- (a) immersion of the whole film for a period of 24 hours;
- (b) swab-rolling on the surface of the film for periods of one, three and five minutes.

Following the treatment the samples were vacuum dried at 10 mm Hg pressure for up to five days and then conditioned at 54% RH in containers of saturated magnesium nitrate solution for seven days. For thermal analysis

tests, the samples were coated with a thin film of silicone oil (Dow Corning Silicone Fluid 210H/100CS) in order to help retain the moisture content.

## Results and discussion

### *Scanning electron microscopy*

The upper surfaces of the films were examined using a Cambridge Stereoscan 200 before and then several months after treatment. Secondary electron images were recorded using Polaroid Type 53 high contrast SEM 5" × 4" (12.5 × 10 cm) film. Samples were mounted directly on double-sided tape with at least one fractured edge unaffected by scalpel cutting. They were gold coated for three minutes using a Polaron 5200 sputter coating unit.

### Appearance of the untreated control samples

The medium-rich burnt sienna films (Fig. 1) have a rougher surface than the more leanly-bound lead white (Fig. 2). The lead white paint surface shows small undulations and significant dust and dirt before treatment. Similar dirt particles are apparent on the burnt sienna samples, but feature less in the micrographs because of the comparative roughness of the surface.

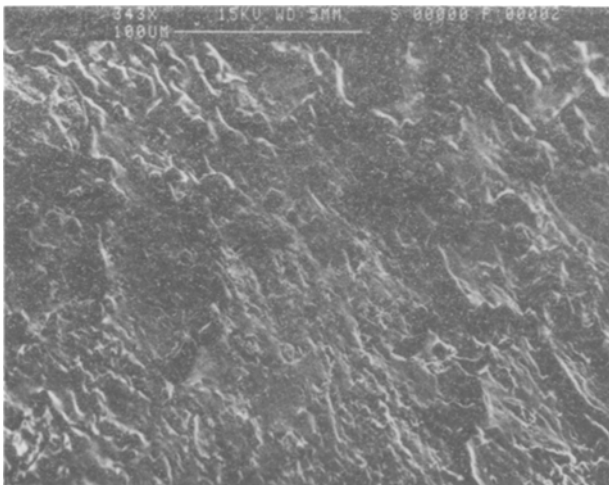


Fig. 1 SEM photomicrograph ( $\times 343$ ) of untreated surface of burnt sienna/linseed oil film

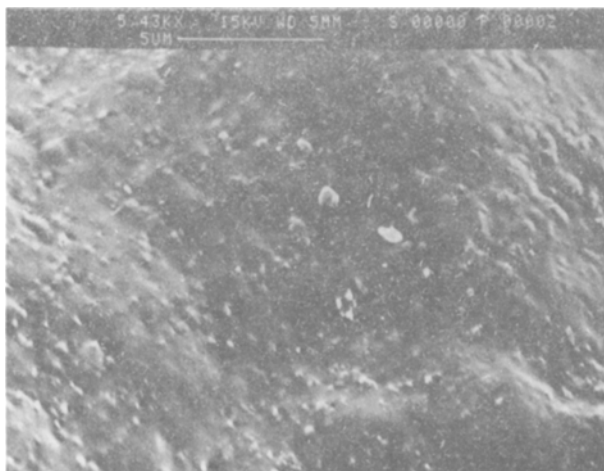


Fig. 2 SEM photomicrograph ( $\times 5430$ ) of untreated surface of lead white/linseed oil film

#### The effects of water

Water produced the greatest surface changes in both kinds of paint, both immersion and swab-rolling causing surface changes in the samples. The largest changes resulted from sample immersion; short duration swab-rolling caused similar changes but to a much smaller degree. The magnitude of

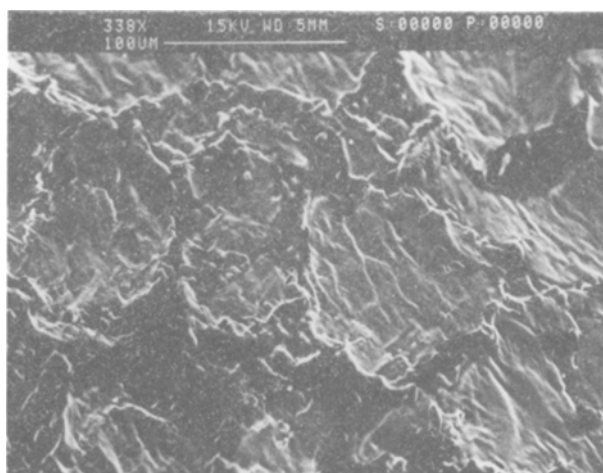
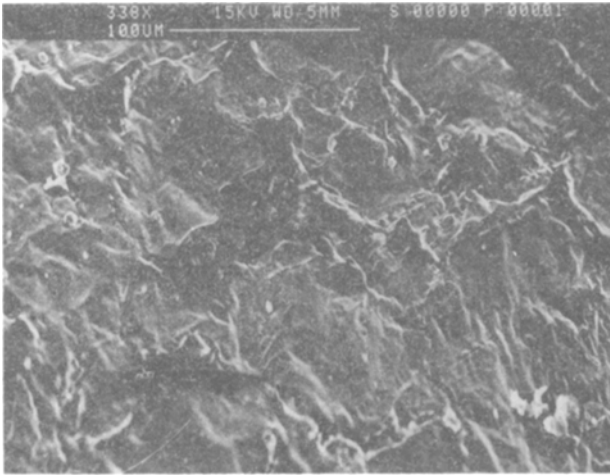
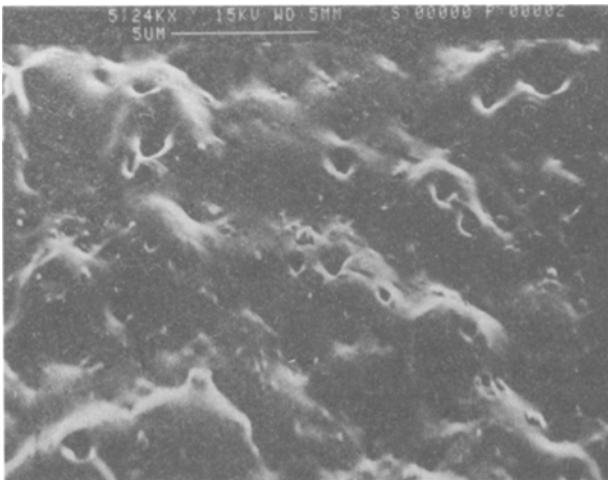


Fig. 3 SEM photomicrograph ( $\times 338$ ) of burnt sienna/linseed oil film after 24 hours immersion in water. Hexagonal crack plates are visible in the medium at the surface

the changes was greatest in the medium-rich burnt sienna: the samples immersed in water formed a roughly hexagonal crack pattern of approximately 100  $\mu\text{m}$  diameter (Fig. 3). The swab-rolled film showed the same effect but much reduced (Fig. 4). The scale of the changes in both cases was such as to produce visible blanching. The effect of the water immersion on the lead

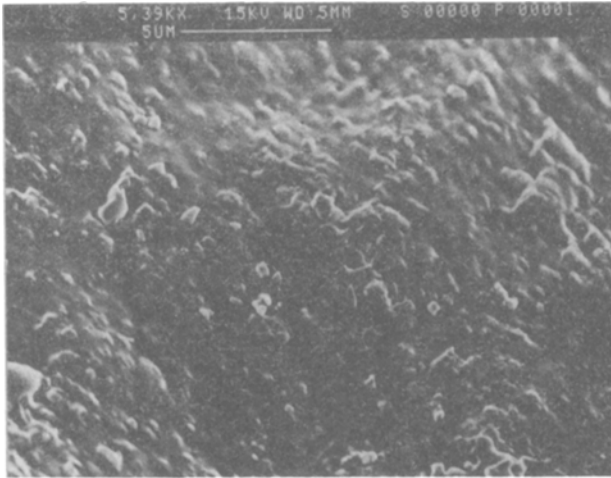


**Fig. 4** SEM photomicrograph ( $\times 338$ ) of burnt sienna/linseed oil film after swab-rolling with water for one minute

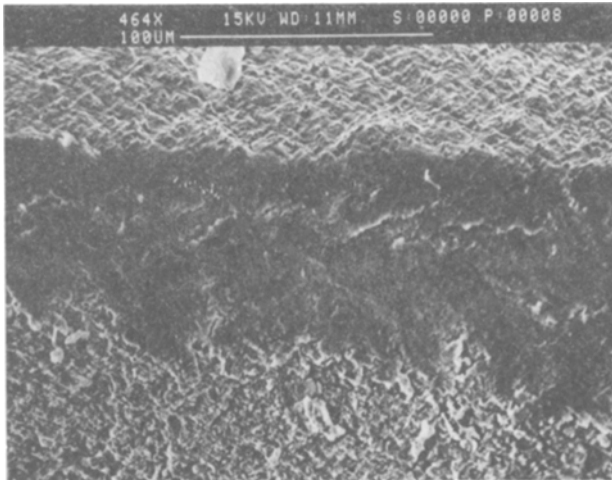


**Fig. 5** SEM photomicrograph ( $\times 5240$ ) of lead white/linseed oil film after 24 hours immersion in water. Surface pores are appearing

white films was not visible to the naked eye, but it did produce pores in the oil medium on the surface, of less than  $1\ \mu\text{m}$  diameter (Fig. 5). Swab-rolling produced relatively little change from the control (Fig. 6). Micrographs

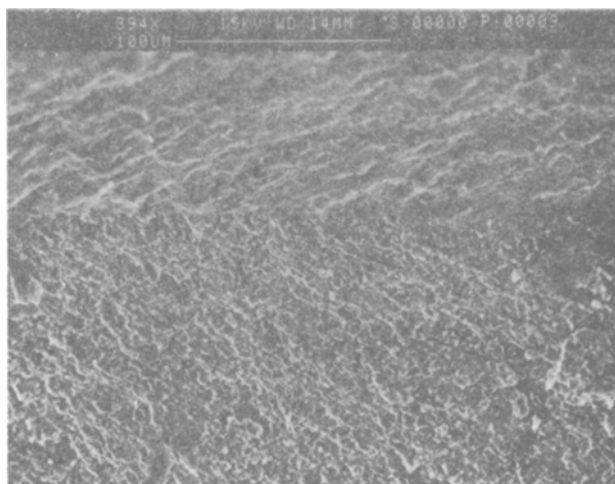


**Fig. 6** SEM photomicrograph ( $\times 5390$ ) of lead white/linseed oil film after swab-rolling with water for one minute



**Fig. 7** SEM photomicrograph ( $\times 464$ ) of cross-sectional profile of a fractured edge of a lead white/linseed oil film after 24 hours immersion in water. In addition to pore formation on the surface, there is a change in density of the paint at the outer edge

taken of the fractured cross-sectional edge of the immersed sample show a change in density of the paint film to a depth of approximately  $10\ \mu\text{m}$  (Fig. 7), whereas a similar profile of the swab-rolled sample shows that the visible effect of the water is confined to about  $3\ \mu\text{m}$  depth (Fig 8).



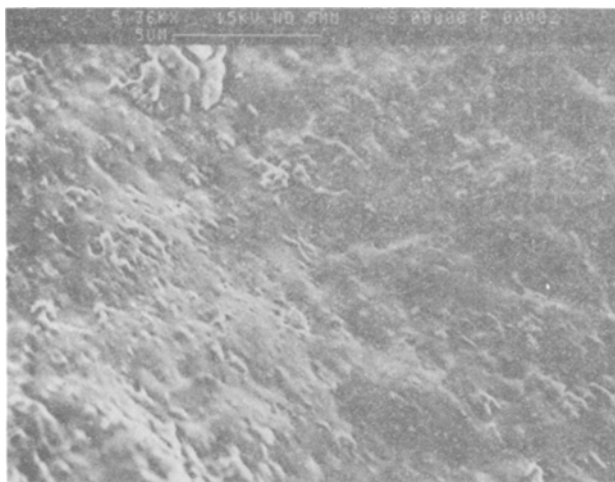
**Fig. 8** SEM photomicrograph ( $\times 394$ ) of cross-sectional profile of a fractured edge of a lead white/linseed oil film after swab-rolling with water for one minute. The changes affect the surface to a depth of a few microns

#### The effects of solvents on the paint films

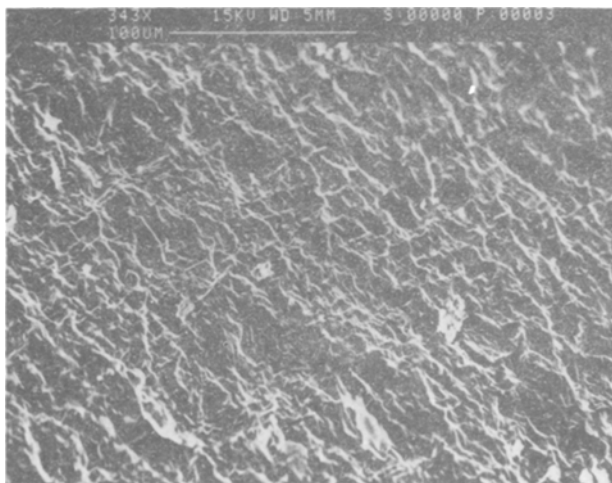
The surface characteristics of the lead white films swabbed with white spirit, methylbenzene, propan-2-ol and propanone differed little from the untreated control. Samples immersed in all of the above solvents, except propanone, did not differ significantly from the control in surface appearance. In the case of propanone immersion, the sample was free of surface dirt and had a smoother, more even surface than the control. This change could have been produced by swelling and reforming of the oil medium, causing it to rise to the surface of the paint. Swab-rolling with propanone had shown the same tendency (Fig. 9). The effects of propanone were larger on the medium-rich burnt sienna films and were more akin to surface etching. Both immersion and swab-rolling with propanone produced an increase in the surface roughness of the paint (Fig. 10). The roughness appeared to be caused by the erosion of the medium at the paint surface.



This change could be explained by the greater accessibility and larger amount — of the medium.



**Fig. 9** SEM photomicrograph ( $\times 5360$ ) of lead white/linseed oil film after swab-rolling with propanone for one minute



**Fig. 10** SEM photomicrograph ( $\times 343$ ) of burnt sienna/linseed oil film after swab-rolling with propanone for one minute. There is some erosion of the medium at the surface

*Thermomechanical analysis (TMA)*

Thermomechanical analysis with constant load was performed using two instruments, a Stanton Redcroft TMA 691 and a Perkin Elmer TMA 7. The samples were subjected to a load of 100 mN with probes of area 1 mm<sup>2</sup>. The temperature was increased at the rate of 5° per minute. Generally between five and seven samples were tested for each condition and the average presented.

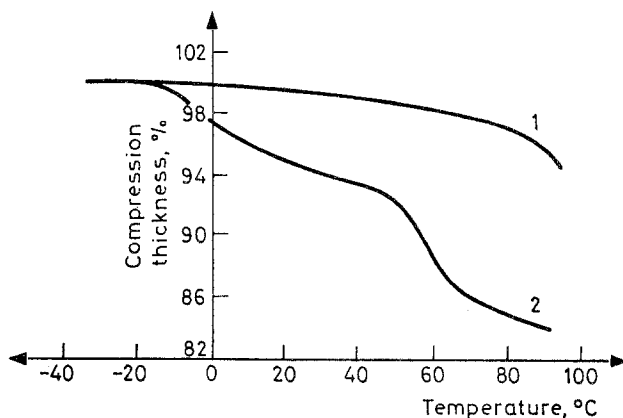


Fig. 11 TMA compression curves for the control samples: (1) lead white, (2) burnt sienna

Figure 11 shows the compression curves for the control samples of burnt sienna and lead white, obtained using the TMA 691. It is apparent that the two films have very different compressibility. The strong-drying, lean-medium, lead white film is much more rigid; for instance, it shows only around 2% compression at 30° compared to about 6% for the burnt sienna film. These differences might be expected since the paints can be considered as instances of high and of moderate degrees of filling of the linseed oil with pigment. Highly filled polymers tend to be more rigid and this effect will be enhanced by the more extensive cross-linking likely to be found in lead white paint. Less predictably, it is possible to discern two distinct softening transitions in the medium-rich burnt sienna, one occurring below 0° and the other occurring in the region from 50–70°. The lead white sample appears to have only one, rather broad region of softening with a poorly defined onset at 40°.

Figure 12 shows how the properties of the burnt sienna film were modified by 24 hours of immersion in water, propan-2-ol and propanone. Immersion in water has produced a curve which is softer than that of the control. However, in the case of the two organic solvents, the film has be-

come much stiffer. Propanone and propan-2-ol immersion produced films which not only showed about three times less compression at 90° than the control but also appeared to show only one broad softening transition commencing between 10 and 20°. This change is no doubt due to the leaching of low molecular weight plasticizing components from the film, resulting in a film whose rigidity had become much closer to that of the lead white control.

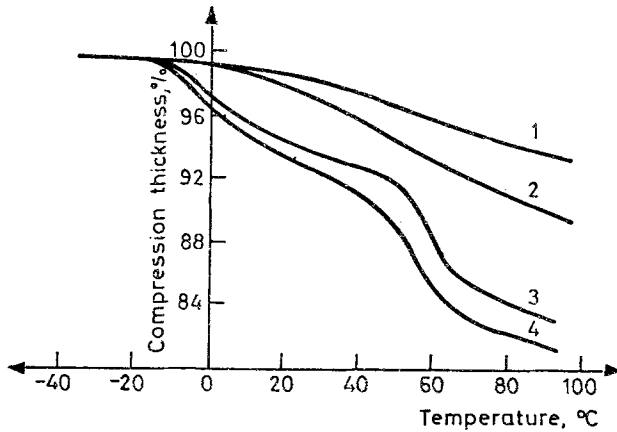


Fig. 12 TMA compression curves for the control and burnt sienna immersion samples: (1) propanone, (2) propan-2-ol, (3) control, (4) water

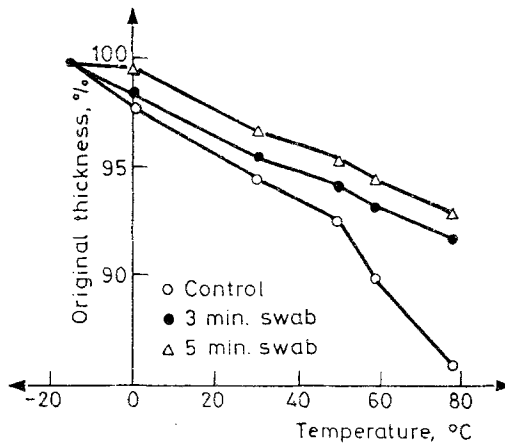


Fig. 13 TMA compression curves for the burnt sienna/propan-2-ol swab-treated samples

Figure 13 shows the influence of swabbing the burnt sienna film with propan-2-ol for three and five minutes. Swabbing for these periods, like immersion, produces substantially leached films. Indeed the five-minute swab

effect is not so different from that of 24-hour immersion. In part, this may be accounted for by the fact that during immersion there was no agitation or flushing of the sample. In swabbing, the effects of rolling and swab capillarity will enhance the rate of removal of leachable components. On the other hand, it is important to emphasize that the spread of curves obtained by swabbing tended to be wide. The grouping improved as the swabbing times were increased from one minute to five minutes. Possibly, short-duration swabbing is a rather unpredictable process, heavily dependent on factors such as access to the medium on the surface, and rolling pressure.

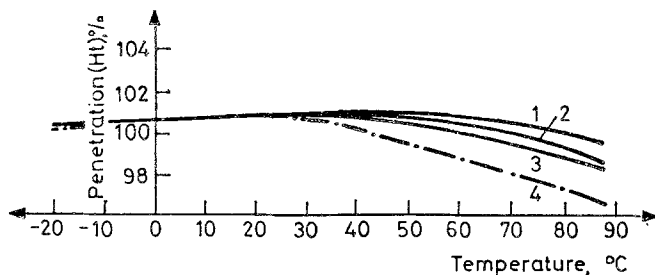


Fig. 14 TMA compression curves for the lead white immersion and swab-treated samples: (1) propanone, (2) propanone one-minute swab, (3) propan-2-ol, (4) control. Helium purge gas

Figure 14 shows the data obtained from the TMA 7 for the lead white control, lead white immersed in propan-2-ol and propanone, and lead white swabbed with propanone for one minute. The control sample is very similar to that determined with the TMA 691 (Fig. 11). The propanone-immersed sample is the most rigid and shows an onset of softening shifted to around 60°. The propan-2-ol immersion and the propanone swab samples show intermediate rigidity and are rather similar to one another. It is interesting to compare the plasticizing effects of the leachable components removed by solvents with those of moisture. Figure 15 presents TMA curves for some lead white/linseed oil paint equilibrated to relative humidities of 5%, the control value of 54%, and 94%. Moisture can be regarded as a plasticizer whose removal results in stiffer films with higher softening temperatures.

Though the TMA data is informative as to the general rigidity and softening of these small samples, it does not provide any indication of the internal relationship between viscous and elastic behaviour, and it does not always resolve transition phenomena clearly.

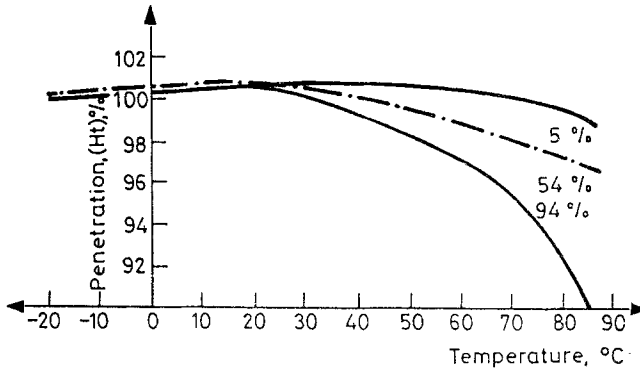


Fig. 15 TMA compression curves for lead white/linseed oil samples equilibrated to relative humidities of 5%, 54% and 94%. Helium purge gas

*Dynamic load thermomechanical analysis (DLTMA)*

Dynamic load thermomechanical analysis (DLTMA) was carried out with the apparatus Model TMA 40. Mettler TMA with an oscillating load of 0.25

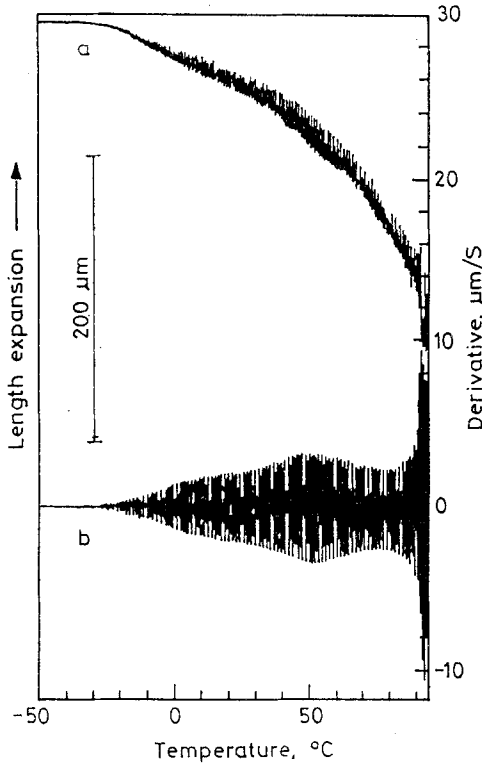


Fig. 16 (a) Dynamic load (DLTMA) curve for the control burnt sienna sample. (b) First derivative of the DLTMA curve for the burnt sienna control sample

$\pm 0.2$  N was used to examine the sample of burnt sienna over the temperature range  $-50^\circ$  to  $100^\circ$ . Figure 16a shows the effect on a film of burnt sienna which had been previously conditioned at 54% RH. As the sample is heated from its glassy state at  $-50^\circ$  it undergoes softening in three stages, at  $-20^\circ$ ,  $28^\circ$  and  $55^\circ$ . The increasing magnitude of the imposed oscillating deformations helps to identify the onset of the softening points. This is more clearly shown in the first derivative curve Figure 16b. The transition at  $-20^\circ$  can be attributed to the glass transition temperature ( $T_g$ ) of linseed oil itself [6], and the origin of the other two transitions is not clear at this stage. Multiple transitions have also been reported in zinc oxide alkyd films [7].

Figure 17 shows that in the water-immersion sample there is an initial hardening which shifts the first transition to a higher temperature. However, by the time the temperature has reached  $45^\circ$  the sample has become less rigid than the control. Consideration of the SEM micrographs (Fig. 3) could suggest that the fractured film tends to compress more on heating. Propanone immersion samples also raise the first transition temperature, but they show an overall increase in rigidity.

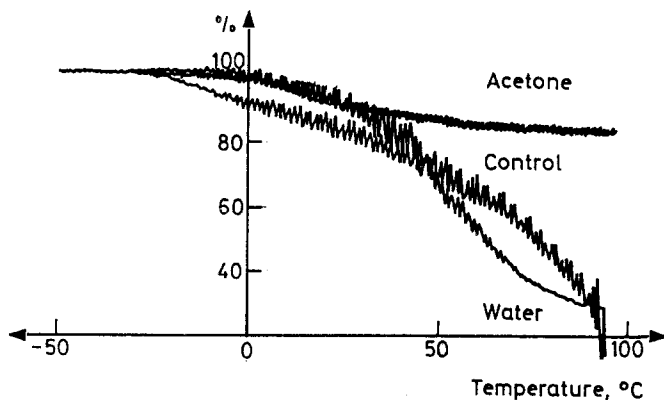


Fig. 17 DLTMA curves of the burnt sienna samples

### *Visco-elastic behaviour*

DLTMA data identified the  $-20^\circ$  change in the burnt sienna film as the major change from an elastic to a visco-elastic state. In polymeric materials 5 regions of visco-elastic behaviour have been identified [8] (Fig. 18);

1) The glassy region, or pre- $T_g$  stage, where the polymer is hard and brittle and shows restricted molecular motion.

2) The glass transition region which corresponds to onset of long range co-ordinated molecular motion and is accompanied with a large change in the stiffness of the samples.

3) The rubbery plateau region which corresponds to the range where polymers exhibit long range rubber elasticity. If they are cross-linked they will retain their rubber elasticity. If they are not cross-linked they will continue to soften.

4) Rubbery flow region

5) Liquid flow region

Characteristic parameters of visco-elastic properties of materials are the storage shear modulus ( $G'$ ) the loss modulus ( $G''$ ) which are a function of frequency and temperature and  $\tan \delta$  which is the ratio of  $G''/G'$ .

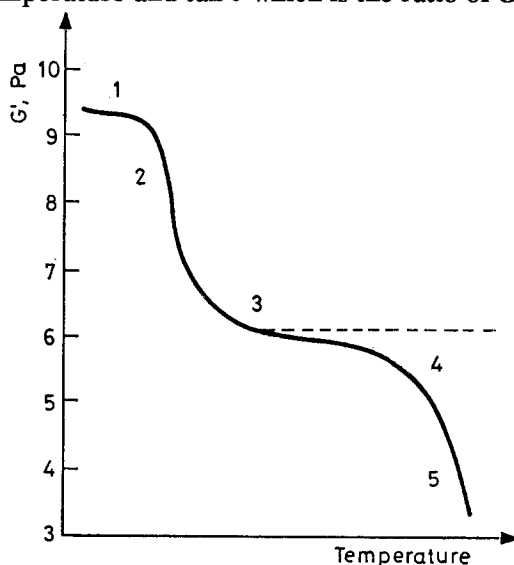


Fig. 18 Regions of visco-elastic behaviour (the dotted line shows the effect of cross-linking)

The shear modulus  $G'$  can be considered as representing that portion of the material which responds elastically to the applied load.  $G''$  represents the tendency of the material to dissipate energy through a viscous response. The ratio of the loss modulus to the storage modulus is termed  $\tan \delta$  and can be seen as an indication of the relative proportions of elastic to viscous behaviour. For example, in a polymer, in the glassy state, the value of  $\tan \delta$  will be very small [9], whereas, in the glass transition region and on the following rubbery plateau,  $\tan \delta$  will be much larger.

It has been established [10] that the greater the cross-linking density, the higher the glass transition temperature, and the smaller the change in  $G'$ ,  $G''$  and  $\tan \delta$  with temperature (Fig. 19).

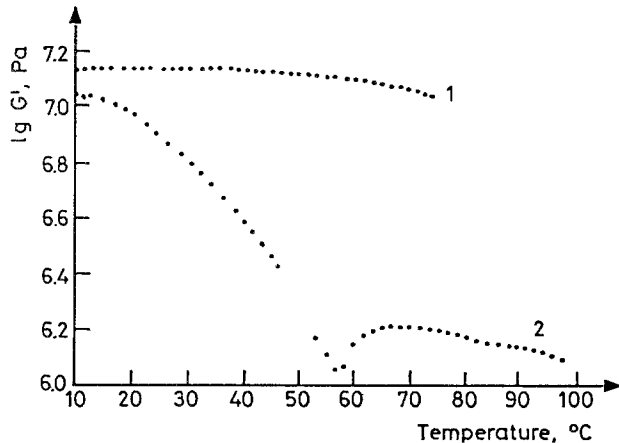


Fig. 19 DMA curve for control samples: (1) lead white, (2) burnt sienna

It is thought that the leachable components of oil paint act as plasticizers [10]. In general, a plasticizer lowers the values of  $G'$ , and decreases the transition temperature while broadening the transition region (Fig. 20). There is an accompanying increase in  $G''$  and the magnitude of  $\tan \delta$ . The actual width of the transition region depends further on the concentration and solubility of plasticizer in the polymer.

Hence in the reverse process of leaching, where loss of plasticizer occurs, the polymeric matrix hardens, and one would expect an increase in  $T_g$  in the system, accompanied by an increase in  $G'$  and a decrease in  $G''$ .

Pigments can also affect the visco-elastic [11] properties of the paint films by reinforcing the matrix (Fig. 21). As the volume fraction of pigment increases then the fall of  $G'$  with temperature above the  $T_g$  is smaller and  $\tan \delta$  decreases.

#### *Dynamic mechanical analysis (DMA)*

##### Control sample of burnt sienna

Samples were examined using the PL Thermal Sciences Dynamic Mechanical Analyser in shear mode at frequencies of 1 and 10 Hz.



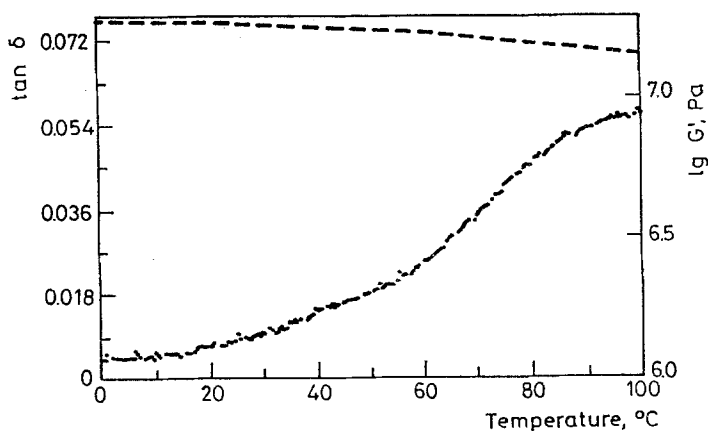


Fig. 20 DMA curves for the burnt sienna/linseed oil propanone-immersion sample

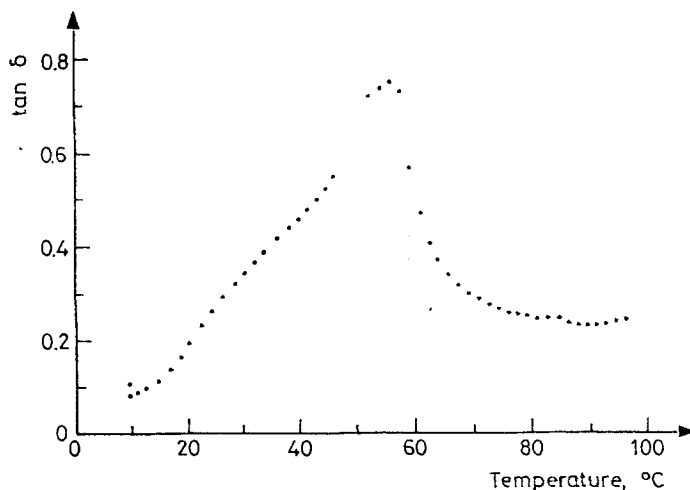


Fig. 21 DMA curve showing the  $\tan \delta$  peak of the burnt sienna control sample

Measurements were made from 5–100° since difficulties were encountered with measurement in shear when starting at lower temperatures. So the DMA measurements begin in a post  $T_g$  region of the medium.

Increase in the temperature causes the material rapidly to soften. The steep decrease in the shear Modulus ( $G'$ ) may indicate that the system is lightly cross-linked in comparison with lead white, where the fall off in the  $G'$  is much smaller, although the different degrees of filling need also to be borne in mind (Fig. 19). There is a very well defined peak of  $\tan \delta$  at 55°. Its value of up to 0.75 shows that the control has a very high component of viscous response [9].

### Effect of water on burnt sienna

The effect of water is to cause an even steeper decline of  $G'$  compared to that of the control. This agrees with the DLTMA observations.

### Effect of propanone and propan-2-ol on burnt sienna

The  $G'$  value of solvent treated immersion samples shows very small variation with temperature (Fig. 20). This indicates that the overall structure is much stiffer and points to the fact that the solvents have leached out plasticizing materials from the cross-linked matrix. Even samples which had been swab rolled for 1 min with propanone showed hardening and the disappearance of the transition at  $55^\circ$ . The  $\tan \delta$  values of around 0.01 are much smaller than for the control, and there is no longer a clear peak.

### *Dielectric thermal analysis (DETA)*

The TMA curves for lead white show that there is a softening of the paint film which occurs in the region of about  $40^\circ$  for the control sample.

It is clear, however, from the TMA and DMA data, that in lead white the region of softening  $40-50^\circ$  is not well-defined in comparison to burnt sienna, where the control sample shows a transition at  $55^\circ$  as a  $\tan \delta$  peak (Fig. 21). DETA measurements were made to investigate further the lead white paint.

The dielectric technique studies the behaviour of materials when subjected to an oscillating electric field, of known frequency, and a controlled temperature programme. The technique detects changes in molecular motion with temperature and frequency and provides a sensitive means for the study of glass and secondary transitions.

A necessary requirement is that the changes must involve dipole activity or charge displacement [12]. Since dielectric measurements are very sensitive to the presence of small quantities of dipolar and ionic species, it was thought that a change in the nature of surface polar groups brought about by water and solvent treatment could be more sensitively detected by DETA.

Characteristic parameters which are measured by DETA are the following:

$\epsilon'$  Permittivity of the sample, which refers to the ease of orientation of dipoles under the action of an applied electric field.

$\epsilon''$  Dielectric loss of the sample, which is a measure of the diffusion of bound charge, or molecular dipole moments, which occurs as a result of the applied field.

$$\tan \delta = \epsilon'' / \epsilon'$$

The effect of propanone on lead white is also more clearly seen through the changes in the height of the  $\tan \delta$  peak. Figure 22 shows that there is a reduction in the  $\tan \delta$  peak for the propanone immersion sample. The decrease in height of  $\tan \delta$  is accompanied by a decrease in the capacitance of the propanone immersion sample. This decrease indicates that the nature of the leached material is polar. If the plasticizer had not been polar then no visible decrease would have been observed. Instead, there would only have been a shift in the  $T_g$  to higher temperatures as observed in the mechanical data. Here in the DETA measurements, in addition to the decrease in capacitance, there is also a shift of the softening to a higher temperature.

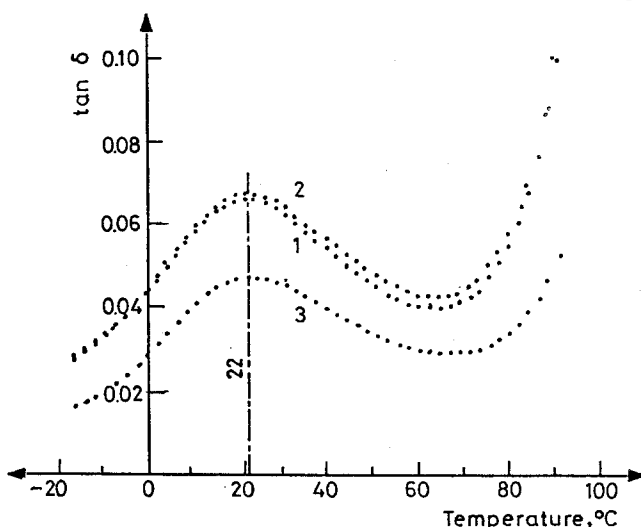


Fig. 22 DETA curves of lead white/linseed oil: (1) untreated control, (2) propanone immersion, one minute, (3) propanone immersion, 24 hours

### Diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS)

The surface of the control and treated paint samples were examined by Fourier transform infra-red spectroscopy since it is recognised that the technique has great potential for gaining information on surface modification [13].

FTIR spectra were recorded in the Diffuse Reflectance mode. The technique of diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS) is based on the combination of absorption and diffuse reflection of infra-red radiation and involves the measurement of the latter. The reflectance spectra were then converted to Kubelka-Munk units which are

directly proportional to the concentration of the scattering medium. Using this algorithm it was thus possible to obtain, non destructively, a measure of the actual decrease in the components on leaching of the paint films.

The Perkin Elmer 1710 FTIR spectrometer equipped with a standard TGS detector was used to record the spectra at  $4\text{ cm}^{-1}$  resolution. Samples were placed directly onto the surface of the mirror used to optimize beam intensity and the cell was purged with  $\text{N}_2$  gas.

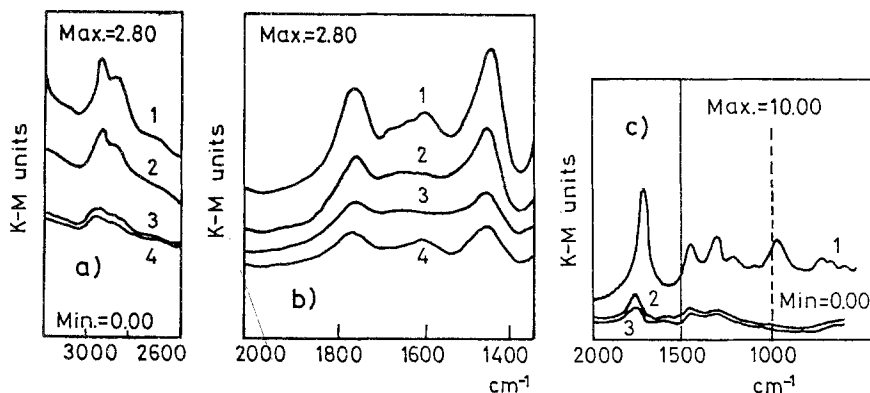


Fig. 23 FTIR diffuse reflectance spectra. (a) & (b) Lead white/linseed oil control and immersion samples: (1) control, (2) white spirit, (3) water, (4) propanone, (c) Burnt sienna/linseed oil: (1) water immersion (similar to control sample), (2) propanone, one minute swab, (3) propan-2-ol, one minute swab

The infra-red spectra (Fig. 23(a) and (b)) of the lead white immersion samples and in particular that of the propanone sample (Fig. 23(b) Spectrum 4) show a decrease in the three major spectral regions:

- 1) The split peak  $2965$  and  $2853\text{ cm}^{-1}$  (Fig. 23a)
- 2) The peak at  $1776\text{ cm}^{-1}$  (Fig. 23b)
- 3) The peak at  $1452\text{ cm}^{-1}$  (Fig. 23b)

The peak at  $1776\text{ cm}^{-1}$  has already been identified as that which is characteristic of aged oil samples [16] and is also present in lead white linseed oil films but absent in haematite linseed oil films where the only characteristic peak is that of the triglyceride ester linkages which appears at  $1746\text{ cm}^{-1}$  [14]. Present studies have shown that untreated burnt sienna linseed oil paint films do show the  $1746\text{ cm}^{-1}$  peak. However, in propanone immersion this peak is not observed. It is replaced by a peak at  $1776\text{ cm}^{-1}$  (Fig. 23c). Indications are that the effect of propanone is to replace the triglyceride ester linkages by oxypolymerised triglyceride components [15].

The peak at  $1452\text{ cm}^{-1}$  is characteristic of carboxylic acid vibrations [14]. Its reduction in the propanone immersion sample indicates the possible loss of carboxylic acids which are polar materials and would explain the decrease in the capacitance and  $\tan \delta$  peak as observed in the DETA measurements (Fig. 22).

## Conclusions

The present work has shown that leaching of the paint films by organic solvents is accompanied by a change in the stiffness of the material which in the case of burnt sienna linseed oil is most pronounced since after treatment it becomes similar to the control lead white samples. Even swab treatment of the burnt sienna causes pronounced effects. The lead white sample showed similar changes on a reduced scale. Water treatment tended to cause softening of the paints. Both TMA and DMTA detected these phenomena on small samples. The DMA data provided additional information on the viscous response of the materials. It has also been demonstrated that DETA measurements are sensitive to changes in the paint films which are caused by a reduction in the number of polar groups originally present. FTIR has provided additional information on the nature of the groups which are lost during the leaching process.

Overall the measurements have emphasized the importance of having complementary techniques in this difficult area of investigation. Above all, they have shown that the methods can be applied to small samples which opens the way for studying samples from paintings and with other cleaning agents.

\* \* \*

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**Zusammenfassung** — Mittels einer Reihe von thermomechanischen und dielektrischen Verfahren sowie FT-IR-Spektroskopie und Scanning-Elektronenmikroskopie wurden die mechanischen und Oberflächeneigenschaften von mit organischen Lösungsmitteln und Wasser behandelten Anstrichfilmen untersucht. Nach der Behandlung konnte eine Veränderung der Oberflächenbeschaffenheit beobachtet werden. Der Effekt von 24-stündigem Eintauchen in bzw. paar minütigem Abtupfen mit Wasser, Propan-2-ol und Propanon (Azeton) von natürlich gealterten, 12 Jahre alten Proben von Bleiweiß/Leinöl und gebrannter Sienaerde/Leinöl konnte als Funktion des Schubmodulus des Anstrichfilmes gemessen werden, begleitet von einem Übergang von viskosen zu elastischen Komponenten in jedem System. Im allgemeinen wurden die lösungsmittelbehandelten Proben härter und wiesen weniger viskose Bestandteile auf, während die wasserbehandelten Proben weicher wurden. Es trat auch eine Änderung der dielektrischen Eigenschaften der ausgelagten Filme auf, was auf den polaren Charakter des Auslaugungsvorganges hinweist. FT-IR Remissionspektren bekräftigten diese Schlußfolgerung.