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Evaluation of the effects of environmental conditions and preventive conservation treatment on painting canvases[1]

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Abstract

The use of preventive conservation measures to assist in retarding the deterioration of painting canvases has been suggested by the Conservation Department of the Tate Gallery [S. Hackney and T. Ernst, The applicability of alkaline reserves to painting canvases, in Preventive Conservation Practice, Theory and Research, Pre-prints of the contributions to the Ottawa Congress, 12–16 September 1994, Ottawa, Canada, p. 223–227]. The reverse sides of paintings are treated with commercially available methoxy magnesium methyl carbonate (MMC) solution. The aim of this paper is to describe how dynamic mechanical thermal analysis can be used to evaluate the effects of this treatment. Measurements are described on modern commercially primed canvas samples [N. Wyplosz, S. Hackney and J.H. Townsend, Studies on the deacidification of canvas with methoxy magnesium carbonate (MMC), in pre-prints of the European Commission research workshop "Effects of the Environment on Indoor Cultural Property", p. 30.] which show that the MMC treatment does affect the mechanical properties of the treated canvas samples and that dynamic mechanical thermal analysis (DMTA) is a suitable technique for its evaluation. The treatment appears to produce a coating on the samples which acts as a moisture barrier. This was also found to occur for treated historic samples (Battelle process) from loose-lining canvases removed from 19th century paintings. The response of the MMC treated materials to variations in relative humidity has also been studied and indications are that their response to variations in relative humidity differs from those of the untreated canvases. © 1997 Elsevier Science B.V.

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1. Introduction

A traditional canvas support normally consists of stretched linen fabric, onto which is brushed an aqueous size of rabbit skin glue. An oil (or more recently, acrylic) ground is then applied. In the twentieth century, cotton canvas has become very popular, sometimes painted directly (unprimed). In the past, lining and relining were processes chosen to conserve the supports of deteriorated paintings. Starches, animal glues, wax mixtures, synthetic polymers in solution or dispersions have all been used as adhesive with varying degrees of success. A variety of rigid and stretched supports has been employed. Application and bonding of adhesives require the use of solvents, water or heat, individually or in combination. In addition, the paint may be subjected to general or localised pressure leading to such effects as the flattening of impasto or canvas weave emphasis.

Inevitably, methods of preventing deterioration are sought. The benefits of preventing canvas from deteriorating lie not only in avoiding the consequences of attempts to correct canvas failure, but also in preventing secondary effects on the painting composite. The

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principle constituent of both linen and cotton is cellulose. Linen contains a greater proportion of lignified material that has survived the retting process. This imparts strength and colour, but makes the linen more prone to deterioration.

Factors which contribute to deterioration of canvases can be summarised as follows: light, external pollution and to a lesser extent, the volatile acids trapped within a frame enclosure. Established museum practice is to keep paintings in air-conditioned galleries in controlled light (150–200 lux) and filtered air [1]. Most canvases are not normally exposed to light, except when removed from their frames, for photography or conservation treatment. But paintings with canvas exposed in the composition do not fit well with this practice since, ideally, they should be lit at minimal levels for viewing, i.e. 50–80 lux, depending on the need for ambient lighting, similar to those for works on paper. The principal pollutant gases in urban areas are sulphur dioxide (SO_2) and nitrogen oxides (NO_x) [2]. Concentrations, particularly of nitrogen oxides which are produced by internal combustion engine exhausts are increasing in some urban areas [2]. Nitrogen dioxide is both an acid and an oxidising agent, contributing to ozone generation. Both SO_2 and NO_2 survive long enough in the atmosphere to enter galleries at significant concentrations, presenting a threat to the objects within [3]. The SO_2 and NO_2 can be removed effectively by adsorption within air-conditioning systems but such filtration is expensive. More simply, air pollution can be excluded from paintings by enclosing their frames with well-sealed backboards and glass [4].

In this case, though the extreme effects of light and external pollution have been prevented, there remains the lesser risk of internal pollutants such as volatile acids trapped within the frame enclosure which can also cause damage. Here, careful selection of materials and possibly the inclusion of carbon filters or other adsorbing materials is required.

Preventive measures will reduce the rate of deterioration of a canvas but natural ageing processes will eventually cause it to oxidise. Studies of paper and linen show that the products of oxidation of cellulose are carboxylic acids, which can then catalyse hydrolysis of the cellulose [5]. In the dark, oxidation is much reduced and hydrolysis becomes the main mechanism of deterioration. It has been shown that cellulosics removed from dark storage and exposed to light, then returned to store, degrade at a higher rate than previously (photo-tendering). The elimination of acid oxidation products reduces considerably the rate of deterioration in the dark [6].

For prints, drawings and water-colours on paper, the best approach is to wash out free acid. For most paintings this is not possible. An alternative is to neutralise acidity within the canvas by application of basic or alkaline material. This is the process normally referred to as deacidification. One material, methoxy magnesium methyl carbonate (MMC) has received most attention because it is readily available and relatively easy to apply. Sold under the trade names of Wei T'o and pHizz, it can be regarded simply as a vehicle for the application of magnesium carbonate in methanol, further diluted with volatile fluorocarbons. When the solvent evaporates, MMC is rapidly converted to magnesium carbonate which remains as the alkaline reserve. The material is applied by brushing or spraying and a judgement must be made between the need to achieve good penetration and safety of the paint film.

To-date, no investigation has been made into the effect of MMC on the mechanical properties of canvas. The aim in this paper is to describe how dynamic mechanical thermal analysis can be used to evaluate the effects of the MMC treatment initially on modern primed and unprimed canvas samples, and 19th century primed canvas samples.

2. DMTA technique

DMTA provides a measure of the viscoelastic properties of the material. Measurement of these properties can be made over a temperature range or isothermally. The technique can also be used in the TMA mode, where changes in the displacement can be monitored. Details of the equipment and methodology are given elsewhere [7].

The parameters measured by the instrument are log storage modulus (Log E'/(Pa)), which is a measure of the stiffness of a material, and tan δ, which gives a measure of the degree of elasticity of the material. The changes in the displacement under given strains can be measured. By measuring artificially aged and historic canvas samples, information can be obtained on the

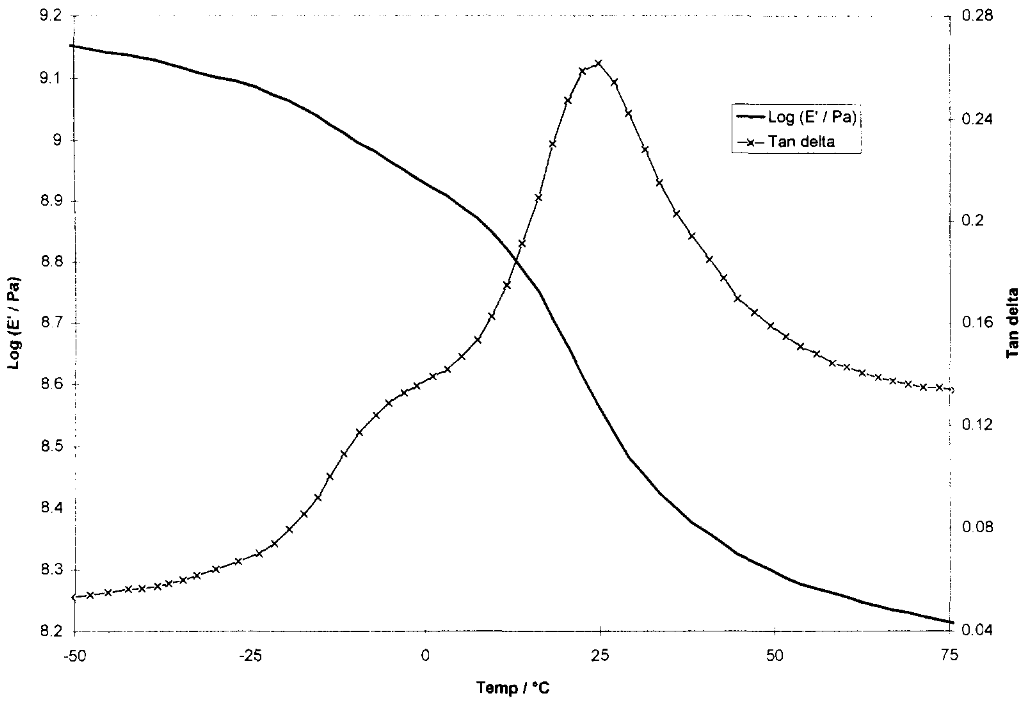

Fig. 1. Typical DMTA curve for an unaged commercial oil-primed canvas.

mechanical properties of actual paintings. Fig. 1 shows a DMTA curve for oil-primed canvas. This represents a typical trace for a sample of unaged oil-primed canvas [7]. Typical values for this sample are as follows: at 25°C (1 Hz) the major tan δ transition has a peak magnitude of $\approx$0.25. The corresponding log storage modulus is $\approx$8.5.

Fig. 1 shows that, at room temperature, the modulus of the sample decreases; i.e. the sample becomes soft. This is confirmed by the fact that the tan δ peak has a maximum in this region.

3. Samples

Primed (Superfine Linen, Universal Primed) and unprimed canvas (Superfine Artists' Linen L 184) were obtained from Russell and Chapple (London). Unaged and artificially aged Cremnitz oil primed samples were provided by the Conservation Department of the Tate Gallery. Samples of printed loose-lining canvas which had been removed from J.E. Millais' "Christ in the House of his Parents" (1849–50), Tate Gallery (NO3584) and from J. Singer Sargent's "The Black Brook", Tate Gallery (NO4783) were also provided by the Conservation Department of the Tate Gallery. Samples of the Millais and Sargent primed canvases which had been deacidified using the Battelle process were also provided.

4. Experimental

4.1. DMTA measurements

In these measurements use was made both of the bending and tensile modes of measurement as previously described [7].

4.2. Ageing of test samples

Samples of Cremnitz oil primed canvas were aged under controlled conditions at the Conservation Department of the Tate Gallery (17 and 34 days heat and light ageing at levels of 20 000 lux, temperature of 60°C and RH 50%).

4.3. Testing effects of relative humidity

4.3.1. Unprimed canvas (Thermal studies)

Samples of untreated and treated (sprayed and brushed) canvases were measured in the tensile mode of the DMTA, in both warp and weft directions. A sample of about 20 mm long × 4 mm wide was cut in either the warp or weft direction from the selected canvas sample using a sharp blade. A dynamic mechanical test was performed on each sample from −25° to 75°C at 3°C/min in the tensile mode, at a frequency of 1 Hz.

4.3.2. Controlled RH conditions on unprimed canvas (Isothermal studies)

Samples of untreated and treated (sprayed and brushed) canvas were held at 30°C in the tensile mode of DMTA instrument under controlled humidity conditions. The test is designed to monitor the change of modulus with RH with respect to treatment. A sample of 20 mm long × 4 mm wide was cut in the weft direction from the selected canvas sample using a sharp blade. A tensile dynamic mechanical test, at a frequency of 1 Hz, was performed on each sample while the temperature was held at 30°C.

The sample humidity was controlled by passing air, (which had been previously bubbled through a Dreschel bottle containing a known sulphuric acid/water mixture) through the gas port of the DMTA measuring head. Three different conditions were used which approximated to 50%, 75% and 100% RH. Each sample was initially exposed to the starting value of ca. 50% RH and allowed to equilibrate. Once the modulus value was steady, the higher values of ca. 75% and 100% bottle were used.

4.3.3. Creep study of unprimed canvas (Isothermal studies)

Tests were carried out on the untreated and treated (brushed and sprayed) unprimed canvas samples at 30°C and a static load of 0.05 N. Each sample was soaked in water overnight prior to measurement. This test was designed to follow the loss of moisture from a canvas as the canvas dried. A sample of about 20 mm long × 4 mm wide was cut in the weft direction from the selected canvas sample using a sharp blade. A tensile creep test,

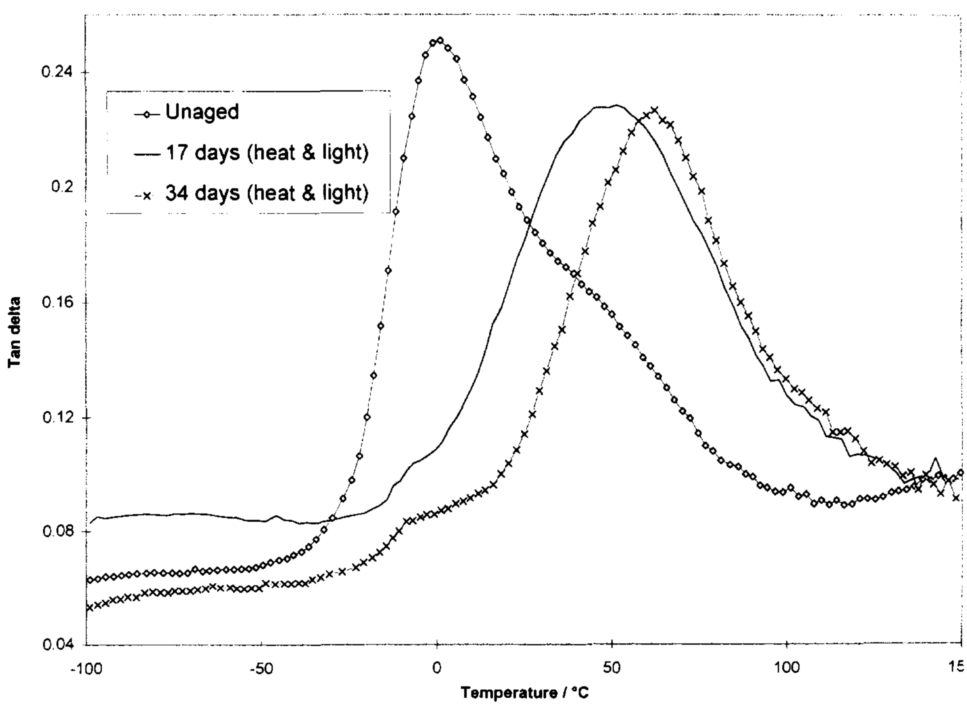

Fig. 2. Effect of artificial ageing on Cremnitz oil-primed canvas (tan δ).

with a static load of 0.05 N, was performed on each sample while the temperature was held at 30°C.

4.3.4. Primed canvas (Isothermal studies)

A sample of the Superfine Linen Universal primed (acrylic based) canvas was measured isothermally at 30°C. The sample was allowed to equilibrate in static air, about 55% RH for 6 h. Flowing air at ca. 80% RH was then passed through the system for 4 h. The flowing air was then changed to the lower RH value of ca. 50% RH for 3 h, and then back to ca. 80% RH for a further 3 h. Finally, the flowing air was turned off and the sample was allowed to equilibrate for a further 15 h in static air at about 55% RH.

4.3.5. Primed canvas (Thermal studies)

Samples of untreated and treated (sprayed) primed canvas were measured in the tensile mode of DMTA (at a frequency of 1 Hz) in the weft direction, and after the moisture had been removed by heating the sample to ca. 120°C. A sample of 22 mm long × 4 mm wide was cut in the weft direction from the selected canvas sample using a sharp blade.

5. Results

5.1. Ageing

Fig. 2 shows the DMTA tan δ curves obtained from the aged and unaged samples. From the tan δ information it is possible to see two transitions. A peak in the region of 0°C (1 Hz), which is more intense in the unaged sample, and which reduces its magnitude after ageing. A second transition at in the region of 50°C (1 Hz) which appears as a shoulder in the case of the unaged sample and evolves as a separate peak after ageing.

By comparing the modulus data at 30°C (1 Hz) (below) it is possible to see the increase in stiffness of the material as the sample is aged.

Sample	Log storage modulus [Log (E'/(Pa))] at 30°C
Unaged	8.28
17 days (heat and light aged)	8.67
34 days (heat and light aged)	8.79

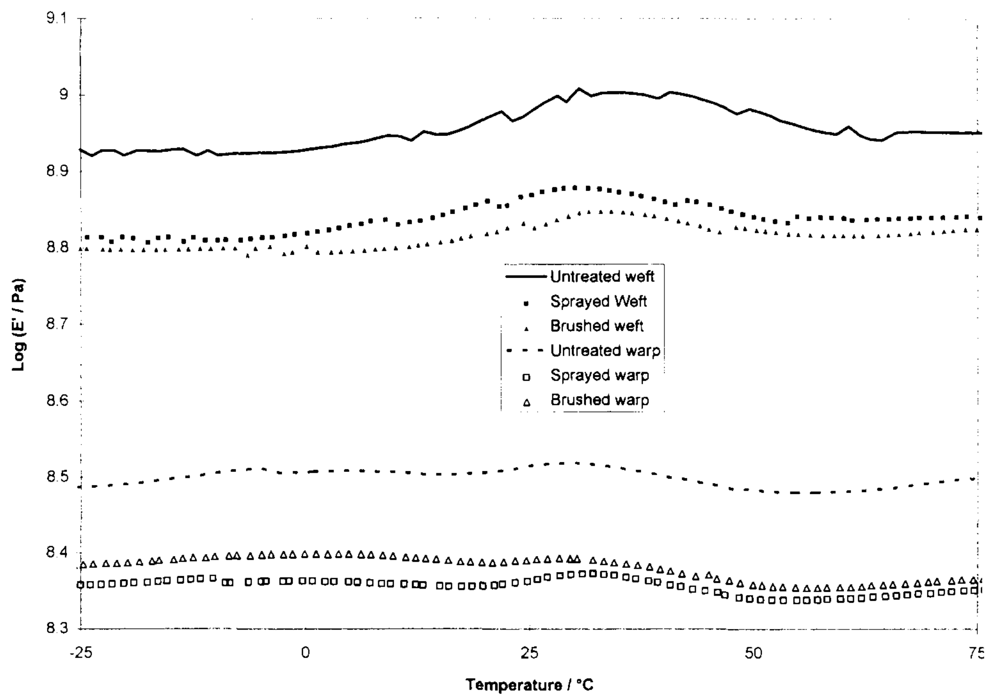

Fig. 3. The variation in the storage modulus Log (E'/Pa) with temperature for both untreated and treated samples of unprimed canvas tested in both the weft and warp directions.

It may be noticed that the mechanical properties are less influenced by ambient temperature variation because of the shift to higher temperature of the major peak. However, the subambient transition has reduced in magnitude with ageing, suggesting that the material is becoming more brittle. Basically the sample is stiffer, more stable and more brittle.

5.2. Relative humidity

5.2.1. Unprimed canvas (thermal studies)

Fig. 3 shows how values of storage modulus Log (E'/(Pa)) vary with temperature for untreated, brushed and sprayed samples. The top three curves correspond to the weft directions of the three samples measured, and the lower three curves correspond to the warp directions.

Each direction is showing the same effect, with regard to treatment. The untreated sample always has the higher storage modulus (stiffness) value and the brushed/sprayed samples have similar, but lower values.

The higher values of modulus collected in the weft direction are due to the instrument measuring along the length of the fibres, in each cloth, rather than the matrix of the material in the warp direction. In both warp and weft directions, the results clearly show that treatment causes a decrease in stiffness.

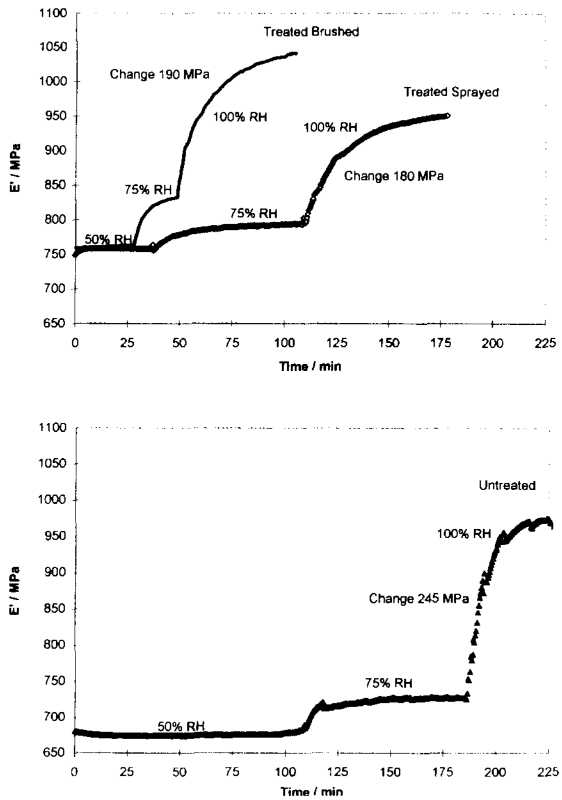

Fig. 4. The variation in the storage modulus E'/(MPa) with time for unprimed canvas samples exposed to increasing levels of relative humidity.

5.2.2. Controlled RH conditions on unprimed canvas (isothermal studies)

Fig. 4 shows the variation in the storage modulus E'/(MPa) with time. Samples were initially equilibrated at ca. 50% RH. The most obvious differences are reflected in the changes observed when samples were exposed to changes in relative humidity from ca. 75% to ca. 100%. The resulting change in modulus is shown on the graph for each sample. In the case of the untreated canvas it is clearly greater and also occur faster than for either the brushed or the sprayed sample, the results indicate that the treatment is creating a partial moisture barrier in the brushed and sprayed samples.

5.2.3. Creep study of unprimed canvas (Isothermal studies)

Fig. 5 shows the change in displacement (expressed in micrometers) which occurs during the drying of the sample under the action of a static load as a function of time (in minutes). The results show that the loss of moisture from untreated samples occurs more rapidly than in the case of the treated materials. The MMC treatment has effectively produced a coating on the samples which acts as a partial moisture barrier.

It is interesting that there is a difference in time and amount of displacement between the sprayed and the brushed samples. Moisture is being retained for longer periods in the case of the brushed sample than it is in the case of the sprayed and the untreated samples. Differences in the amount of displacement also indicate that there is a difference in the extent of overall effect on the mechanical properties caused by the different methods of application (spraying or brushing).

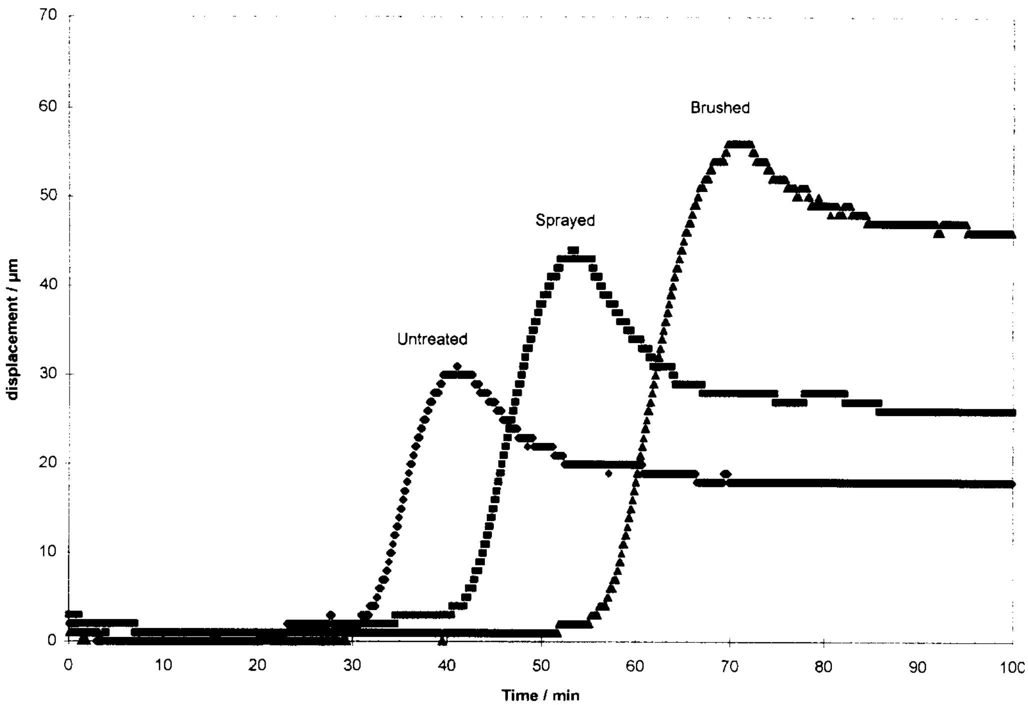

Fig. 5. The change in displacement /(µm) which occurs during drying of unprimed canvas samples under the action of a static load as a function of time.

5.2.4. Primed canvas (thermal studies)

Fig. 6 shows results on samples which have been initially dried. There is a lowering of the magnitude of tan δ throughout the temperature scan for the treated material. In other words, the samples become more elastic after treatment.

5.2.5. Primed canvas (isothermal studies)

The effect of changing the relative humidity on the primed canvas can be seen clearly in both tan δ and log storage modulus traces (Fig. 7). On increasing the RH there is an almost immediate increase in stiffness which is maintained while the higher RH is held. However, tan δ initially shows an increase, followed by a gradual decrease, finally equilibrating at a level lower than the original value. This would suggest that the fibres in the canvas initially undergo some rapid change which causes the matrix to be distributed. After a period of rearrangement, the fibres eventually form a more elastic structure. The reverse of this process occurs when the RH is reduced. When the air flow was stopped the same effects were observed but over a much longer period of time.

5.2.6. 19th century painting canvas (thermal studies)

Fig. 8 shows the effect of soaking the sample from the printed loose-lining canvas removed from Sargent's painting. There is a lowering in temperature of the tan δ peak which corresponds to a softening of the material. The deacidification treatment retards the plasticising effects of water indicating that probably less penetration or wetting occurs. The treated sample shows a small reduction in the tan δ peak position and a minor decrease in the modulus with respect to the untreated sample, and suggests that the deacidification process has created a partial moisture barrier.

6. Conclusions

Results show that the MMC treatment affects the mechanical properties of the treated canvas samples, and that dynamic mechanical thermal analysis is a suitable technique for the evaluation of the effect of the treatment. The MMC treatment produces: (1) a change in the stiffness of the samples which depends on the environmental conditions; and (2) appears to

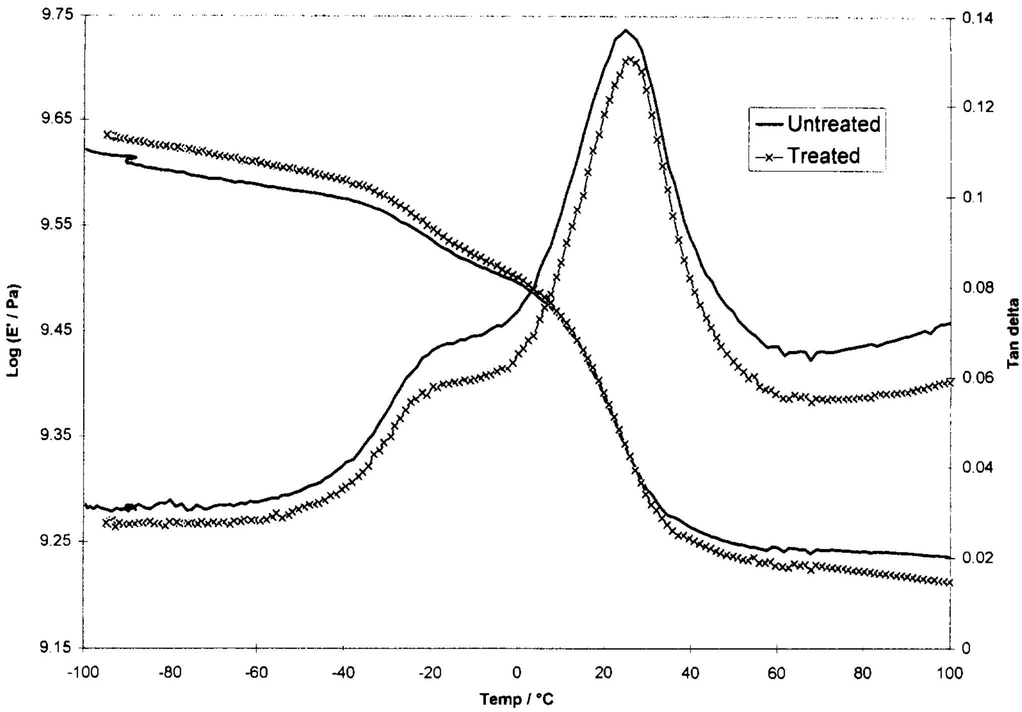

Fig. 6. The effect of pre-drying acrylic- primed canvas samples (untreated and spray-treated) on the variation in Log (E'/(Pa)) and tan δ over the −100–100°C range.

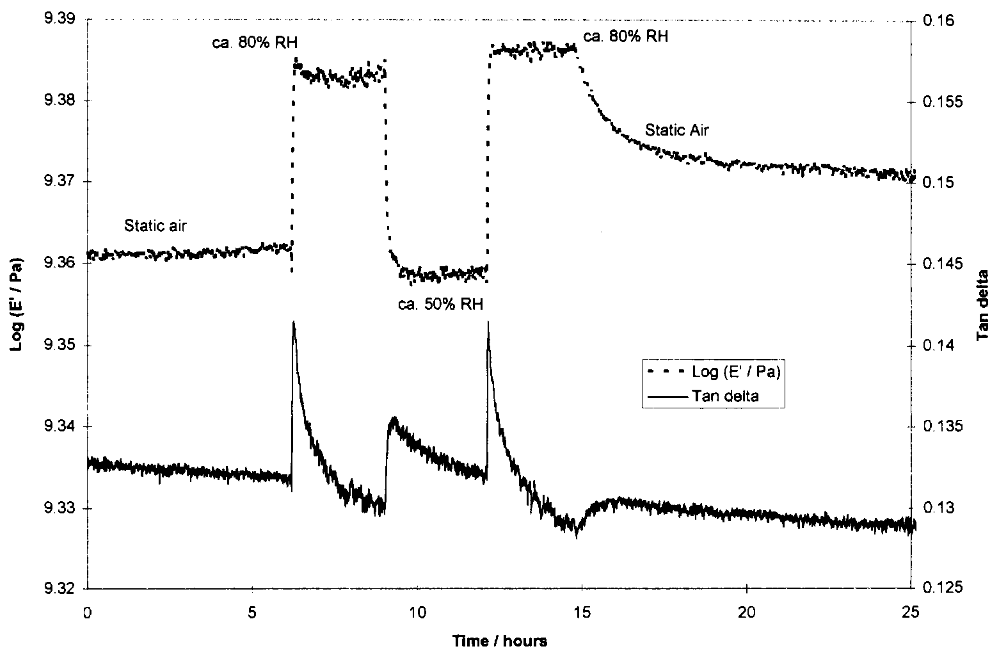

Fig. 7. The effect of varying the RH on an acrylic primed canvas at constant temperature of 30°C [tan δ and Log (E'/(Pa))]

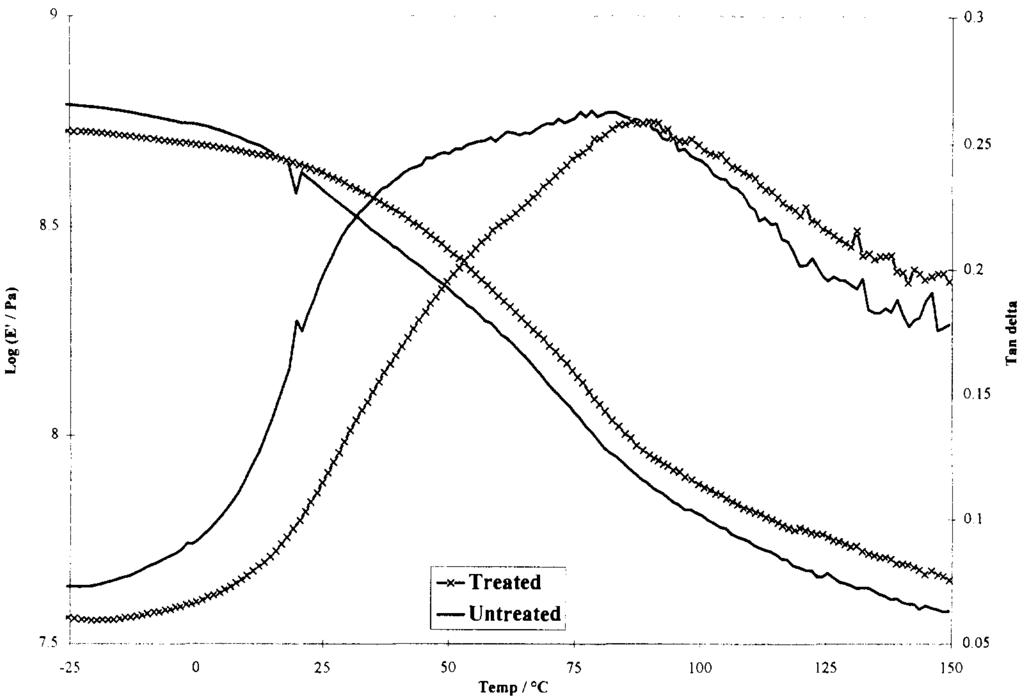

Fig. 8. The effect of soaking treated and untreated printed loose-lining canvas removed from Sargent's painting (Tate Gallery NO4783) on log (E'/(Pa)) and tan δ.

produce a coating on the sample, including the historic canvas, which acts as a moisture barrier and which influences the further response of these samples to fluctuations in relative humidity.

The DMTA measurements also reveal differences in response to relative humidity changes depending on whether samples have been treated either by brushing or spraying. In Fig. 4, for example, there are differences in the magnitude of the change in the modulus values and response times for sprayed and brushed samples. In Fig. 5 the loss moisture for the brushed sample takes longer than for the sprayed or the untreated samples. In the case of the primed canvas samples, the differences between treated and untreated samples as measured in the bending mode as a function of temperature are not as obvious.

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