DYNAMIC MECHANICAL THERMAL ANALYSIS FOR THE EVALUATION OF DEACIDIFICATION TREATMENT OF PAINTING CANVASES

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Abstract

The use of non-aqueous deacidification procedures as a preventive conservation measure to assist in retarding the deterioration of painting canvases has been suggested by the Conservation Department of the Tate Gallery [1]. The reverse sides of paintings are treated with commercially available MMC solution (methoxy magnesium methyl carbonate). 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 [2] which show that the MMC treatment does cause an increase in the modulus or stiffness of the primed canvas materials but that the effect on the T_g is minimal. The response of the treated materials to variations in relative humidity has also been studied and indications are that the response of treated canvases to variations in relative humidity differs from those of the untreated canvases.

Keywords: conservation, deacidification procedures, TMA

Introduction

Rationale for deacidification of painting canvases

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

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or dispersion have all been used as adhesives 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 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 [3]. Most canvases are not normally exposed to light except when removed from their frames, for photography or conservation treatment. However, 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, that is 50 to 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) [4]. Concentrations, particularly of the nitrogen oxides, which are produced by internal combustion engine exhausts are increasing in concentration in some urban areas [4]. 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 [5]. They 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 [6]. 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 and 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 cause it eventually 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 [7]. 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-tender-

ing). The elimination of acid oxidation products reduces considerably the rate of deterioration in the dark [8].

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 method, 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 W_{ei} 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. Application is not a simple process. Brushing and spraying are used and 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.

Experimental procedure

Measurement technique (DMTA)

DMTA provides a measure of the viscoelastic properties i.e. the elastic and loss modulus of the material. Measurement of these parameters can be made over a temperature range and isothermally. The technique can also be used in the TMA mode where changes in the displacement can be monitored.
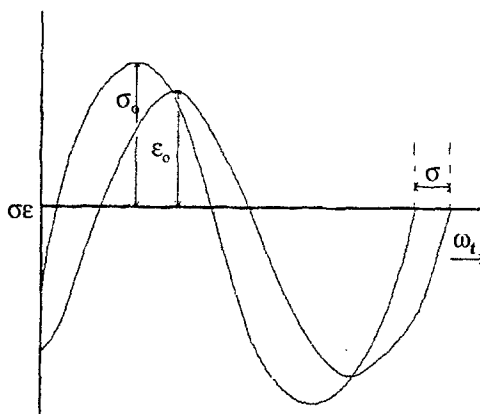

Fig. 1 Sinusoidal stress and strain response in the linear viscoelastic region

The DMTA MkIII apparatus consists of a system controller, analyser, temperature programmer, cryogenic unit and measuring head. A variable amplitude sinusoidal mechanical stress is applied to the sample to produce a sinusoidal strain of preselected amplitude. Figure 1 shows the sinusoidal stress with the strain response lagging by some phase angle because of the viscoelastic behaviour of the sample. The complex modulus E^* has both real and imaginary components, E' and E'' and these are known as the storage and loss modulus respectively. The relationship between the quantities is best summarised in the Argand diagram (Fig. 2).
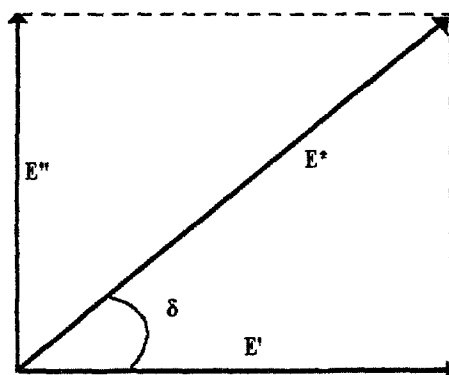

Fig. 2 The complex modulus E^* resolved into real (storage modulus E') and imaginary (loss modulus E'') components as illustrated in the Argand diagram

The DMTA MkIII can also be easily operated in the TMA mode with a sensitivity of up to 1 μm the sample can be measured under a tensile or compressive force of up to 15 N.

In these measurements use was made both of the bending and tensile modes of measurements. The single cantilever bending mode (Fig. 3) was found to be most suitable for the primed canvas materials. The head can accommodate a
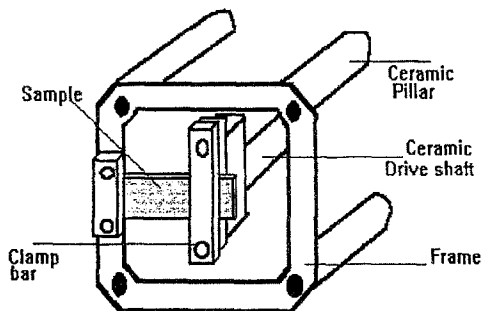

Fig. 3 Primed canvas samples supported for measurement in the bending mode
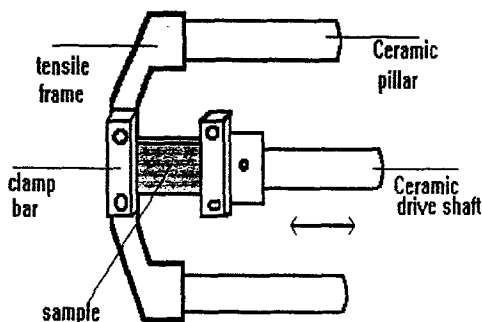
Fig. 4 Unprimed canvas samples supported for measurement in the tensile mode

sample from 1 mm up to 16 mm free length. The sample width can be up to 12 mm with a maximum thickness of 3.5 mm. The Tensile mode (Fig. 4) was used for creep testing. In general this arrangement was most suitable for thin paint films and fibres. These clamps can accommodate a sample from 1 mm up to 30 mm free length.

Samples

Samples of unprimed canvas (Superfine Artists' Linen L 184) and primed canvas (Superfine Linen, Universal Primed) were obtained from Russell and Chapple Ltd. (London).

Unprimed canvas (Thermal scans)

Samples of untreated and treated (sprayed and brushed) canvas were measured in the tensile mode of the DMTA in both warp and weft directions. A sample of approximately 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^{-1} in the tensile mode, at a frequency of 1 Hz.

Controlled *RH* conditions on unprimed canvas (Isothermal scans)

Samples of untreated and treated (sprayed and brushed) canvas were held at 30°C in the tensile mode of the DMTA instrument under controlled humidity conditions The test is designed to monitor the change of modulus with *RH* with respect to the treatment. A sample of approximately 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 bubbling air through a bottle containing a known sulphuric acid/water mixture and then piped through the gas port on the DMTA measuring head. Three bottles were used during the tests giving 50, 75 and 100% *RH* conditions. Each sample was initially exposed to 50% *RH* conditions and allowed to equilibrate. Once the log storage modulus value was steady then the 75% bottle was switched into line and then finally the 100% bottle was used.

Creep study of unprimed canvas (Isothermal scans)

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 approximately 20 mm long×4 mm wide was cut in weft direction from the selected canvas sample using a sharp blade. A tensile creep test, with a static load of 0.05 N, was performed on each sample while the temperature was held at 30°C.

Primed canvas (Thermal scans)

Samples of untreated and treated (sprayed) primed canvas, were measured in the tensile mode of the DMTA in the weft direction. Each sample was measured with no moisture control and after the moisture was removed by heating (moisture was prevented from reabsorbing into the dried material by continually passing liquid nitrogen around the sample chamber).

A sample of approximately 20 mm long×4 mm wide was cut in the weft direction from the selected canvas sample using a sharp blade. A dynamic mechanical test was performed on each sample in the tensile mode, at a frequency of 1 Hz.

One sample was measured under the standard conditions by first cooling the sample to its minimum temperature of −100°C and then collecting data at 3°C min^{-1} up to the maximum temperature of 100°C.

The other sample was first heated to 125°C in order to remove the moisture from the material. The sample was then cooled to −100°C and then data were collected as above.

Primed canvas moisture control (Thermal scans)

A sample of approximately 20 mm long×10 mm wide was cut in the weft direction from the selected canvas sample using a sharp blade. Both samples were immersed in water for 30 s prior to measurement. After removal from the water the excess moisture was removed using a paper tissue. One sample was coated with fomblin oil (a fully fluorinated oil which was used as moisture barrier in

these experiments) and the other left uncoated. A dynamic mechanical test was performed on each sample from −100 to 100°C at 2°C min⁻¹ in the single cantilever bending mode at a frequency of 1 Hz.

Results

Unprimed canvas (Thermal scans)

Figure 5 shows how values of storage modulus ($\log E'$ (Pa)) vary with temperature results for both untreated, brushed and sprayed samples. The top three curves of Fig. 5 correspond to the weft directions of the three samples measured and the lower three curve correspond to the warp directions.
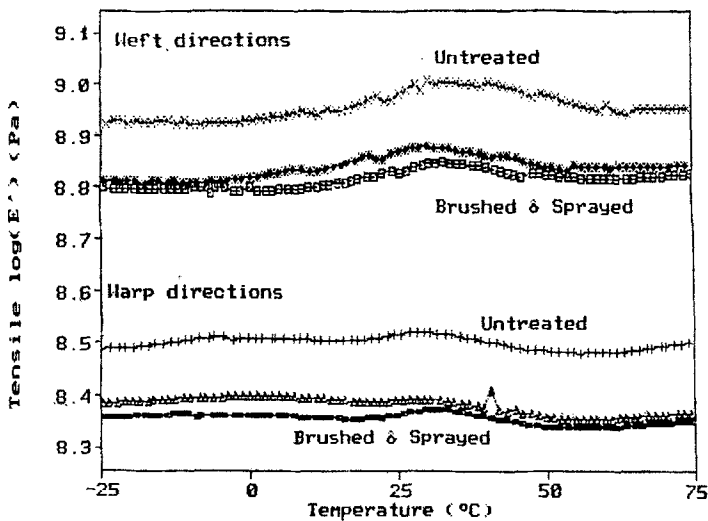

Fig. 5 Variation in the storage modulus ($\log E'$ (Pa)) with temperature for both untreated, and treated samples of unprimed canvas tested in both the weft and warp directions

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 log storage modulus collected in the weft direction are due to the instrument measuring along the length of the fibers, in each cloth, rather then 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.

Controlled RH conditions on unprimed canvas (Isothermal scans)

Figure 6 shows the variation in the storage modulus ($\log E'$ (Pa)) with time. Samples were initially equilibrated at 50% RH (note that the untreated sample

was left for longer period of time at this value). The most obvious differences are reflected in the changes observed when samples were exposed to changes in relative humidity from 75 to 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 occurs faster than the brushed or the sprayed sample. Results indicate that the treatment is creating a partial moisture barrier in the brushed and sprayed samples.
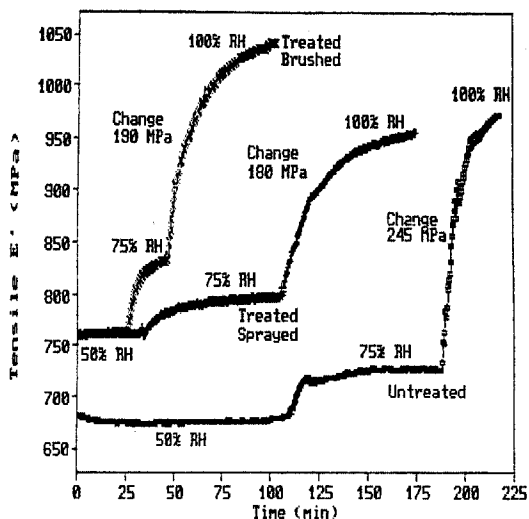

Fig. 6 Variation in the storage modulus (logE' (Pa)) with time for unprimed canvas samples exposed to increasing levels of relative humidity
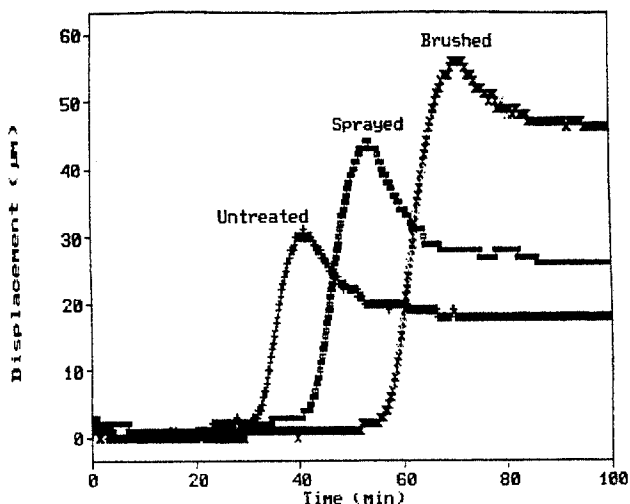

Fig. 7 The change in displacement (μm) which occurs during drying of unprimed canvas samples under the action of a static load as a function of time (min)

Creep study of unprimed canvas (Isothermal scans)

Figure 7 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. The 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).

Primed canvas (Thermal scans)

Figure 8 shows the results on samples with no moisture control and Fig. 9 shows results on samples which have been initially dried and in this way then measured at the same moisture content. Both plots show similar data with respect to treatment. There is a lowering of tanδ throughout the temperature scan for the treated material. Also the effects of moisture in the samples can be seen by comparing the two plots.
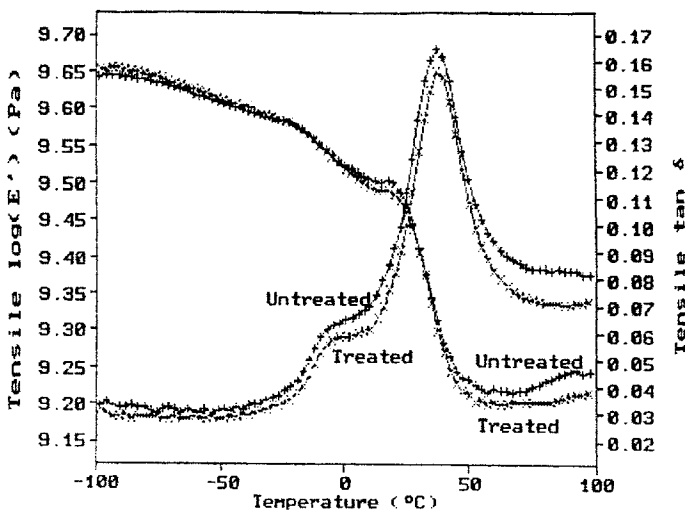

Fig. 8 Variation in logE' and tanδ for primed canvas samples (untreated and spray treated) over the temperature range −100 to 100°C
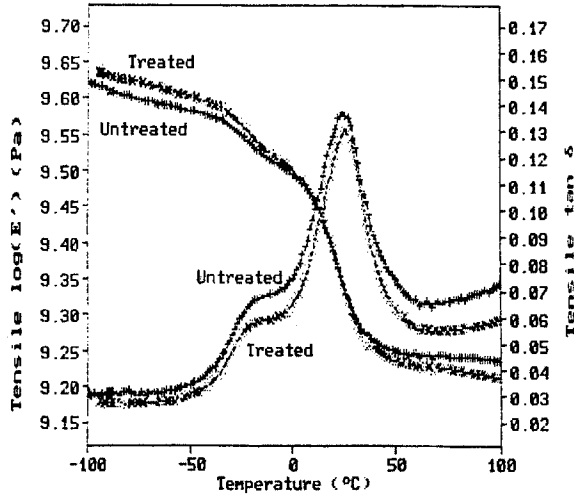
Fig. 9 The effect of pre-drying primed canvas samples (untreated and spray treated) on the variation in logE' and tanδ over the temperature range −100 to 100°C

Figure 9 shows a lowering of the tanδ peak height at approximately room temperature for the dried samples. In Fig. 8 there is moisture loss taking place at around 0°C and above 50°C which can be seen clearly in both the log storage modulus traces.

The tests clearly show that the treatment causes a decrease in tanδ (damping) throughout the temperature range measured. In other words the samples become more elastic after treatment.
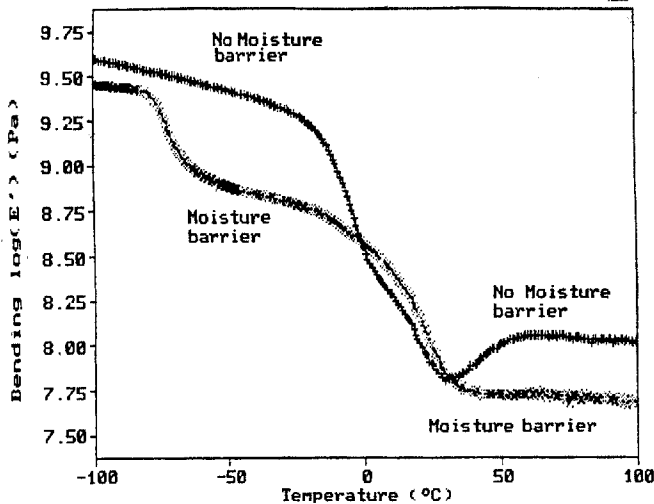

Fig. 10 The effect of a moisture barrier (used to coat the untreated primed canvas samples) on the variation in logE' over the temperature range −100 to 100°C

Primed canvas moisture control (Thermal scans)

Figure 10 shows the log storage modulus plots for both the coated and un-coated samples. The low temperature transition for the fomblin oil is clearly seen at approximately −60°C (1 Hz). Also the loss of moisture can be seen in the uncoated sample starting at approximately 35°C.
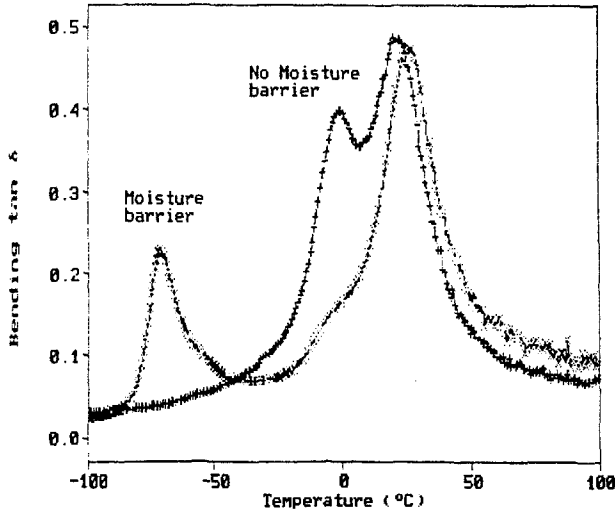

Fig. 11 The effect of a moisture barrier (used to coat the untreated primed canvas sample) on the variation in tanδ over the temperature range −100 to 100°C

Figure 11 shows the tanδ for both samples. The low temperature transition for the moisture barrier at approximately −60°C (1 Hz) and the much larger peak in tanδ at approximately 0°C (1 Hz) can be seen in the case of the uncoated sample.

The results clearly show that the fomblin oil used provided an excellent barrier to the uptake or loss of moisture from the canvas.

Conclusions

Results show that the MMC treatment does affect 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 decrease in the stiffness of the samples, [2] the samples become more elastic, and the treatment appears to produce a coating on the samples which acts as a moisture barrier.

The DMTA measurements also reveal differences in response to relative humidity changes depending on whether samples were treated either by brushing

or spraying. In Fig. 6, 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. 7 the loss in moisture for the brushed sample takes longer than for the sprayed or the untreated samples. In the case of the primed samples the differences between treated and untreated as measured in the bending mode as a function of temperature are not as obvious.

Further measurements are in progress to test the response of the primed samples to variations in relative humidity to determine whether differences such as those for the unprimed samples can be observed. The effect of MMC treatment on artifically aged, naturally aged and historic samples is also under investigation.

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