Journal of Thermal Analysis and Calorimetry, Vol. 90 (2007) 1, 249–253

IMPROVED CONTROLLED TEMPERATURE AND RELATIVE HUMIDITY DMA OF ARTISTS' ACRYLIC EMULSION PAINT FILMS

Part I.

B. Ormsby[1]*, *G. Foster*[2], *T. Learner*[1], *S. Ritchie*[3] *and M. Schilling*[4]

[1]Conservation Department, Tate, London UK
[2]Smithers Rapra, Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK
[3]School of Engineering and Computer Science, Exeter University, Exeter, UK
[4]Getty Conservation Institute, Los Angeles, USA

Issues encountered with dynamic mechanical analysis of artists' acrylic emulsion paint films are presented alongside modifications to improve controlled relative humidity (RH) experiments using isothermal and thermal scanning conditions. Free films of titanium white (PW6) artists' acrylic emulsion paints were cast as free films and their viscoelastic properties measured using the tensile mode of the dynamic mechanical analyser (DMA). Artists' acrylic emulsion paints are within their glass transition temperature region at room temperature and are highly responsive to changes in ambient temperature and relative humidity, hence controlling relative humidity during analysis is vital to the successful analysis of these paints.

Keywords: *acrylic emulsion, dynamic mechanical analysis, films, paint, relative humidity, titanium white*

Introduction

The need to evaluate changes in the physical properties of 'modern' paints that may occur as a result of standard conservation treatments such as surface cleaning, has recently been identified as a priority in cultural heritage conservation and preservation [1–4]. Modern paints, including household, industrial and artists' paints have all been used by 20th and 21st century artists and to date, unlike traditional oil-based paints, there is relatively little information available on their physical properties, how they age under standard museum conditions and their long-term response to conservation treatments.

Within this context, works of art created from artists' acrylic emulsion paints have frequently been identified by conservators as problematic to surface clean. One of the principal reasons for this is that acrylic emulsion paint films have a relatively low glass transition temperature (T_g) of around 10°C, which – while providing excellent flexibility – makes the paint films particularly soft at room temperature, thus facilitating the retention of surface dirt and making the removal of imbibed dirt difficult.

Other concerns include the effects of water – commonly used for surface cleaning – on dried emulsion paint systems and the possible extraction of hydrophilic components from the bulk film. It is important to know whether the loss of these components contributes to any subsequent physical deterioration of the paint films. Recent research has repeatedly shown that polyethylene oxide-based surfactants are extracted by water treatments from these paint films [4–7]. Encouragingly, however, mechanical testing carried out thus far has shown that water-treated acrylic emulsion paint films do not suffer a significant increase in stiffness when subjected to typical conservation treatment exposures [8].

The paint films used for this study were created directly from tubes of professional grade artists' acrylic emulsion paints, liquitex acrylic artists' colours. Titanium white (PW6) was chosen as the pigment because of its ubiquitous use in modern paints and works of art. The titanium white pigment is the rutile form, which is typically treated with a double surface coating of silica and alumina to act as a barrier between this potentially reactive pigment and the acrylic medium. The binder is an acrylic emulsion copolymer of *n*-butyl acrylate/methyl methacrylate; p(*n*BA/MMA), which has been the most commonly used acrylic binder since the 1980s, and displays a T_g of around 10°C. The polymer chains used in emulsion formulations typically possess a broad range of molecular mass values, with the upper end often above the 1 million amu range. In the dried acrylic film, the degree of cross-linking is thought to be relatively low, with dry film insolubility and physical properties primarily being imparted by polymer chain entangle-

---

* Author for correspondence: bronwyn.ormsby@tate.org.uk

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

ment. Under accelerated ageing conditions, a degree of cross-linking has been reported to occur within *n*BA/MMA copolymer films [9, 10], although the progress of this reaction is expected to be minimal under typical museum conditions.

Acrylic emulsion paints also contain a range of other constituents, which are added by both the emulsion and paint manufacturers; however the identity of the majority of these materials remains proprietary information. The authors employed several analytical methods to provide information on the bulk constituents of the paint, such as FTIR (Fourier transform infrared) analysis to identify the p(*n*BA/MMA) copolymer type, fillers and pigments and FTIR-ATR (attenuated total reflectance) to characterise the presence of polyethylene-based surfactants on the surface of, and as – a major constituent present in water extracts of, these paint films. The identification of trace level additives has proven to be more difficult, which is in part due to the poor solubility of dried acrylic emulsion films.

Waterborne paints are susceptible to water absorption, with hygroscopic components such as the non-ionic surfactants remaining trapped within the bulk film as agglomerates as well as exuding to the air and substrate interfaces during the drying process. Water also exists as an independent entity within the polymer film, and as these water domains are connected to liquid water outside the film, they act as channels for water diffusion. The hydrophilic nature of the surfactants suggest that the structures on the film surface may act as potential water diffusion pathways, as can traces of surfactant that may be left in the channels created by water evaporation during drying [11]. The polymer blend composition can also have an effect on water absorption, with a decrease in absorption occurring with an increase in the hard phase of the copolymer, i.e., MMA.

Dynamic mechanical analysis (DMA) has been used to assess the viscoelastic properties such as T_g, storage modulus (E') and tanδ of conservation and cultural materials such as parchment, historic textiles, leather and paper [12–16]. To date, controlled RH DMA has not been employed as part of a cleaning study on artists' paints. For most DMA applications RH is either not controlled, or controlled to a limited extent. Initial testing for this research was carried out using uncontrolled conditions. However, it quickly proved advantageous to use a controlled RH DMA system as designed by Foster *et al*. [17–18]. This paper outlines the results obtained with both uncontrolled and controlled RH DMA and explains the modified system and methodology used as part of wider research into the surface cleaning of acrylic emulsion paints, the results of which are to be outlined in forthcoming publications.

Experimental

Sample preparation

Films were cast onto Teflon coated stainless steel plates using a Sheen instruments film caster to a dry thickness of 110±20 μm. Films were stored in dark ambient conditions and had between 8 and 22 months of natural ageing prior to testing. Samples were preconditioned in a temperature controlled laboratory set at 21±1°C, with ambient RH levels varying between 30 and 75%.

Instrumentation

All analysis was carried out on a Polymer Labs MkIII DMTA instrument in tensile mode. Sample free length was 5 mm from samples measuring 10±0.5 mm wide·22.5 mm total length. For standard DMA, the instrument was in the upright position with a closed oven and a thermal scan from –50 to 120°C at 3°C min^{-1}; frequency of 1 Hz; strain of 2 (32 μm approx. peak to peak); starting load of 0.1 N in reducing force mode; clamps were hand tightened; no averaging with no clamp retightening at low temperature. For the controlled RH experiments the heating rate was reduced to 1.5°C min^{-1}, the thermal scan narrowed to 15 to 60°C, and the RH set at 50% (it was possible to control the RH to a specific value (±2%) in the range between 10 and 80% RH). Frequency was set as 1 Hz; strain of 2 (32 μm approx. peak to peak); starting load of 0.1 N in reducing force mode; clamp torque was 10 cNm; with no averaging and no clamp retightening at low temperature. Data was collected using PlusV version 5.42 and plotted using Origin software version 7.5 (OriginLab Corporation).

Results and discussion

Standard DMA – no RH control

Problems were quickly encountered using the standard DMA system, as the ambient humidity trapped within the oven dramatically affected the data produced. While repeatability was essentially acceptable for several runs carried out on the same day, unacceptable repeatability from one testing period to another highlighted the need to control testing conditions. Figures 1 and 2 include the storage modulus and tan delta (tanδ) data respectively for free films of Liquitex titanium white paint analysed at different periods, with the ambient laboratory RH also recorded. While some of the differences can be accounted for by variations in drying time, the ambient RH of the laboratory has had a marked effect; with the %RSD (obtained by the multiplying the standard deviation

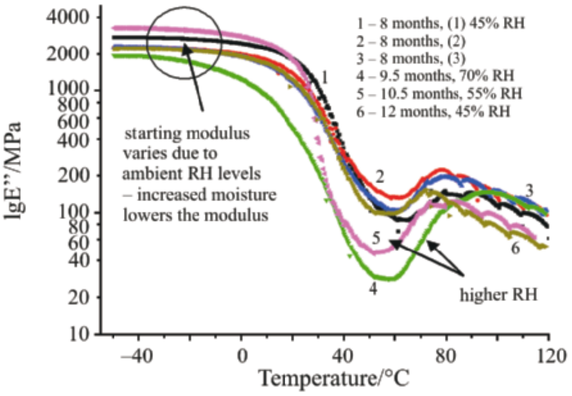

Fig. 1 Storage modulus (*E*’’)–temperature curves for several samples of Liquitex titanium white free-film, controls. Varying drying time and ambient %RH

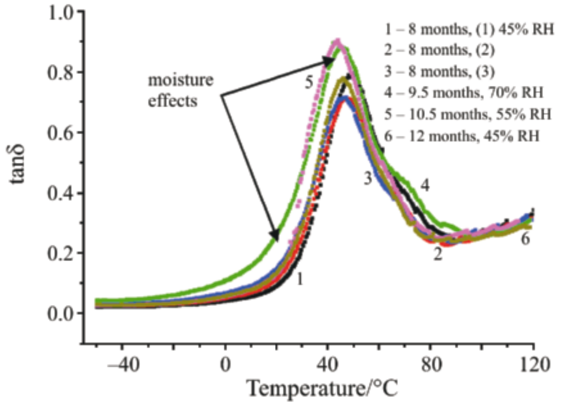

Fig. 2 Tanδ–temperature curves for several samples of Liquitex titanium white free-film, controls. Varying drying time and ambient %RH

by 100 and dividing the average) of the tanδ peak height value at 10.7% or ±10.7% from the average. The increased RH has resulted in a decrease in storage modulus, an increase in tanδ peak height and a shift of the tanδ peak to a lower temperature. These changes reflect an increase in moisture content within the paint films, which will be discussed in more detail in a forthcoming publication.

Figures 3 and 4 clearly illustrate the magnitude of the changes that can occur with variation in paint moisture content as well as DMA oven RH. By drying the films in an oven and maintaining DMA oven dryness with a liquid nitrogen purge during analysis, the modulus and tan delta curves altered significantly from the ambient conditions, with a maximum difference in tanδ peak height of 0.5 between the wettest and driest runs of the same paint. This very clearly illustrates the susceptibility of these paints to moisture permeation and reinforces the necessity to control RH during analysis, particularly when attempting to assess subtle changes in physical properties.

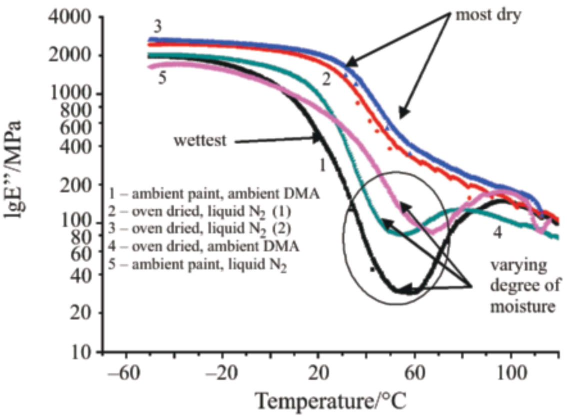

Fig. 3 Storage modulus (*E*’’)–temperature curves for several samples of Liquitex titanium white free-film, controls. Testing conditions varied from most dry – paint dried in oven overnight and liquid N_2 purge during run; to wettest sample – ambient RH in DMA oven and ambient RH preconditioning

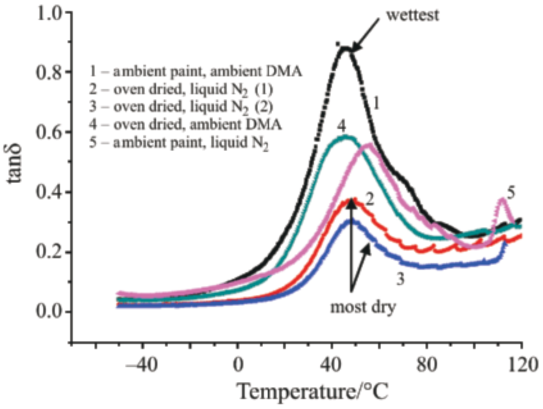

Fig. 4 Tanδ data–temperature for several samples of Liquitex titanium white free-film, controls. The wettest sample has highest tanδ peak height value

Modifications to the DMA–humidity system and sample preconditioning

In order to accommodate the RH/temperature control system, modifications were made, including placing the head of the DMA in an inverted position on a special stand to allow the drive shaft to operate vertically downwards. The drive shaft and supporting pillars were extended by 150 mm and, to accommodate the extended shafts, the furnace lid was removed and automatic operation overridden.

The humidity controlled system illustrated in Fig. 5 [17] essentially consists of a polycarbonate chamber sealed with a rubber washer, with separate dry and 100% RH supplies independently regulated by two valves which are mixed before entering the chamber. Due to safety constraints and limited space,

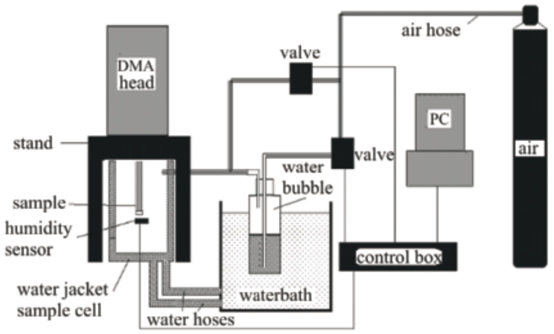

Fig. 5 Schematic representation of controlled relative humidity DMA system

it was not possible to use the DMA oven. Hence, temperature was maintained by surrounding the chamber with a water jacket and by placing the pipe work and bubbler inside a water bath, delivering reliable temperature control within a 10 to 60°C range. To measure and control RH, a sensor was fitted inside the environmental cell and interfaced to a PC that logged and controlled the valves.

In order to minimize variations induced by temperature and RH effects during analysis, the RH was controlled within a ±2% margin throughout the temperature ramp. The heating rate was a constant 1.5°C min^{-1} to 60°C. The RH sensor updated regularly and the software compensated for changes in temperature. It is appreciated that the sample was not able to fully equilibrate with the changing temperature and moisture conditions during a scan; however the purpose was to monitor the relative changes in material properties. To this end as many of the potential variables (sample thickness, heating rate etc.) were fixed. To ensure the paint films had a reproducible moisture content the samples were preconditioned for at least 24 h in a sealed saturated salt chamber fitted with a constant flow fan, set at ~50% RH using saturated magnesium nitrate. Dynamic vapour sorption (DVS) experiments revealed that these paints required 2 h to equilibrate at a particular RH when below 65%. Therefore, 24 h assured equilibration to the required test RH.

To produce dry films, samples were placed into sealed glass jars containing silica gel beads and left for at least 48 h prior to testing to reach equilibrium at ~<10% RH. All samples were transferred as quickly as possible from the humidity chamber to the DMA and allowed to equilibrate within the DMA chamber at the appropriate RH for at least 5 min prior to starting the run. One limitation of this system was the restricted thermal scan range, however the range possible coincided with the region of greatest interest for these paints, i.e. room temperature and the T_g region.

After some experimentation, a single test method involving a thermal scan from 15 to 60°C, with controlled humidity at 50% and 24 h sample preconditioning at 50% was chosen as the experimental standard. Figures 6 and 7 include the results of six DMA runs of the same Liquitex Ti white film analysed under these conditions over two testing periods. Here the average tanδ peak temperature produced a %RSD of 3.39 and the %RSD of the average tanδ peak height was 3.52.

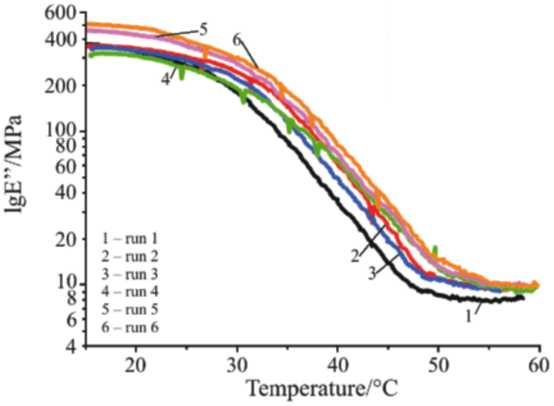

Fig. 6 Controlled RH storage modulus (*E*'')–temperature curves for several samples of Liquitex titanium white free-film, controls. All samples thermally scanned from 15–60şC at 50% RH with overnight sample preconditioning at 50% RH

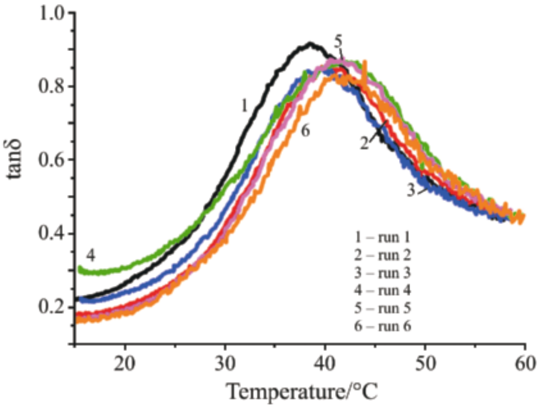

Fig. 7 Controlled RH tanδ curves for several samples of Liquitex titanium white free-film, controls. All samples thermally scanned from 15–60şC at 50% RH with overnight sample preconditioning at 50% RH

Conclusions

Standard mode DMA was unsuccessful for the analysis of artists' acrylic emulsion paint films because RH is a vital parameter to control when analysing such hygroscopic paint films. Uncontrolled RH testing conditions do not produce repeatable results and distortions arising from fluctuating ambient RH levels can mask any subtle changes in physical behaviour that may be significant to the long term behaviour and care of these paint films. Modifications to the DMA system to incorporate RH and temperature control, as well as sample preconditioning to the required test RH produced repeatable results on a consistent basis. A standardised test regime of 50% RH sample preconditioning for 24 h and a DMA run at 50%RH with a thermal scan from 15 to 60°C was determined as an accurate method from which to assess any changes in physical properties resulting from conservation treatments and ageing regimes.

Acknowledgements

The authors would like to acknowledge the generosity of the Leverhulme Trust, who funded 3 years of research at Tate (2002–2006); AXA Art Insurance for providing 3 further years of support for this research (2006–2009); Becker Industrial Coatings for providing the DMA instrument; Getty Conservation Institute for funding DMA analysis; the University of Exeter for awarding Honorary Research Fellowships to both Tate authors; Surface Measurement Systems (SMS) for the DVS tests; ColArt UK for providing the Liquitex paints; and Corus UK Ltd. for the Teflon coated steel substrates.

References

1 T. Learner, The Conservator, 24 (2000) 96.
2 A. Murray, C. C. De Berenfeld, S. Y. S. Chang, E. Jablonski, T. Klein, M. C. Riggs, E. C. Robertson and W. M. A. Tse, Materials Research Society Symposia Proceedings, 712 (2002) 83.
3 E. Jablonski, T. Learner, J. Hayes and M. Golden, Reviews in Conservation, 4 (2003) 3.
4 B. Ormsby, T. Learner, M. Schilling, J. Druzik, H. Khanjian, D. Carson, G. Foster and M. Sloan, Oberflächenreinigung. Materialien und Methoden, VDR Schriftenreihe 2, Ed. Cornelia Weyer, Theiss Verlag, Stuttgart (2006) 135–150.
5 S. Digney-Peer, A. Burnstock, T. Learner, H. Khanjian, F. Hoogland and J. J. Boon, Contributions to Bilbao Congress, 13–17 September 2004. International Institute for Conservation of Historic and Artistic Works (2004), 202–207.
6 J. J. Boon and T. Learner, J. Anal. Appl. Pyrol., 64 (2002) 327.
7 G. D. Smith, ICOM Committee for Conservation 14th Triennial Meeting, The Hague, Preprints. James & James (Science Publishers) Ltd., (2005), pp. 824–832.
8 E. Hagan and A. Murray, Materials Research Society Symposium Proceedings, 852 (2005) 41.
9 T. Learner, O. Chiantore and D. Scalarone, ICOM Committee for Conservation 13th Triennial Meeting Rio de Janeiro, Preprints,. James & James (Science Publishers) Ltd., (2002), pp. 911–919.
10 D. Scalarone, O. Chiantore and T. Learner, ICOM Committee for Conservation 14th Triennial Meeting, The Hague, Preprints. James & James (Science Publishers) Ltd., (2005), pp. 350–357.
11 N. Agarwal and R. J. Farris, J. Appl. Polym. Sci., 72 (1999) 1407.
12 M. Odlyha, R. M. Walker and W. H. Liddell, J. Thermal Anal., 40 (1993) 285.
13 M. Odlyha, G. M. Foster, N. S. Cohen and R. Larsen, ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, James & James (Science Publishers) Ltd., (1999), pp. 702–707.
14 N. S. Cohen, M. Odlyha and G. M. Foster, Thermochim. Acta, 365 (2000) 111.
15 M. Odlyha, N. S. Cohen, G. M. Foster and A. Aliev, ICOM Committee for Conservation 13th Triennial Meeting, Rio de Janeiro, Preprints. James & James (Science Publishers) Ltd., (2002), pp. 615–621.
16 M. Odlyha, Q. Wang, G. M. Foster, J. de Groot, M. Horton and L. Bozec, J. Therm. Anal. Cal., 82 (2005) 627.
17 G. M. Foster, S. Ritchie and C. Lowe, J. Therm. Anal. Cal., 73 (2003) 119.
18 G. M. Foster, S. Ritchie, K. E. Evans and C. Lowe, Progr. Org. Coat., 51 (2004) 244.

Received: June 9, 2006
Accepted: August 7, 2006
OnlineFirst: February 13, 2007

DOI: 10.1007/s10973-006-7724-x