

IMPROVED CONTROLLED RELATIVE HUMIDITY DYNAMIC MECHANICAL ANALYSIS OF ARTISTS' ACRYLIC EMULSION PAINTS Part II. General properties and accelerated ageing

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After improvements were made to a modified Polymer Labs MkIII DMTA instrument to facilitate repeatable controlled humidity (RH) experiments using isothermal and thermal scanning conditions, the viscoelastic properties of titanium white pigmented artists' acrylic emulsion films were measured in tensile mode. The effects of temperature, relative humidity and accelerated ageing regimes on two brands of titanium white paints were explored. These paints are highly responsive to changes in temperature and relative humidity, formulation differences affect properties slightly, and while light ageing had a negligible effect, thermal ageing resulted in decreased storage modulus and increased film density.

Keywords: acrylic emulsion, accelerated ageing, conservation, dynamic mechanical analyser, light, paint, preservation, relative humidity, temperature, thermal, titanium white

Introduction

The need for investigation into the physical properties of artists' acrylic emulsion paints, including their response to ageing, environment and conservation treatments has been established [1–6]. Dynamic mechanical analysis carried out in Part 1 of this study determined that these paints are highly responsive to changes in temperature and relative humidity and demonstrated the need to tightly control these parameters during testing [6]. Part 2 further explores the effect of temperature and relative humidity, the general properties of two titanium white paints and compares the effect of accelerated ageing on several physical properties using a controlled RH DMA system, [6, 7] with the broad aim of exploring the long-term implications for works of art made with acrylic emulsion paints.

The paint films used for this study were cast directly from tubes of professional grade artists' acrylic emulsion paints, Liquitex acrylic artists' colours and Talens Rembrandt colours, as described in Part 1 [6]. These two brands represent the two types of acrylic emulsion copolymer used in artists' paints, i.e. the Liquitex paint is an *n*-butyl acrylate/methyl methacrylate copolymer; p(*n*BA/MMA), the most commonly used acrylic binder since the 1980s. The Talens paint is an ethyl acrylate/methyl methacrylate p(EA/MMA) copolymer, generally used from the early 1960's to the 1980's although still used today by

Talens. The polymers typically possess a broad range of molecular masses, with the upper end often above the 1 million amu range.

So far, there is little evidence of detrimental changes in the physical properties of naturally-aged acrylic emulsion paintings when stored and displayed under appropriate conditions; however these paintings are now at most, approaching 50 years old. While these paints are relatively flexible when compared to oil or alkyd paints, research into the mechanical properties of acrylic emulsion paints has established that these films lose the ability to plastically deform in response to an applied force below temperatures of 5°C at 50% RH, and below 11°C at 5% RH, and that atmospheric water acts as a plasticizer [8–11].

Recent studies involving the accelerated ageing of artists' acrylic emulsion paints and unpigmented acrylic emulsion films have revealed that acrylic emulsion binders are generally highly stable to photooxidation under accelerated light ageing conditions [12]. Within dry acrylic emulsion films, the degree of cross-linking is thought to be relatively low, with dry film insolubility and physical properties primarily being imparted by polymer chain entanglement. Despite this, solubility experiments have repeatedly shown that these paints have an insoluble fraction, which may be due to chain entanglement or cross-linking, or both [12, 13]. Upon exposure to light ageing (UV free) the insoluble fraction tends to in-

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crease slightly for p(*n*BA/MMA) copolymer films, suggesting an increase in cross-linking, and decrease slightly for p(EA/MMA) copolymer films, suggesting chain scission may be occurring. Gravimetric tests carried out by the authors have also revealed that % mass loss during thermal ageing is greater than natural and light ageing, suggesting that components of dry acrylic emulsion paint films are thermolabile.

The advantage of DMA is that one analysis produces several useful pieces of information, including: the storage modulus (E') or stiffness of the paint films; % displacement, which reflects flexibility; T_g , in this case defined as the temperature at the apex of the $\tan\delta$ peak^{**}; and a measure of the film's cross-link density, corresponding to the height of the $\tan\delta$ peak (ν -axis). In addition, the authors have assessed aspects of the chemical composition of each of these paints by using FTIR (Fourier transform infrared) analysis to determine the composition of the acrylic copolymer, the presence of calcium carbonate filler in the Talens paints, and a polyethylene oxide-based surfactant as the major component of water extracts of these films. FTIR-ATR (attenuated total reflectance) analysis was also used to identify the presence of polyethylene oxide-based surfactants on the surface of these films, where the Talens paint films consistently had more surfactant on the surface than the Liquitex films. The authors and others [12–14] have suggested that surface surfactant reduces with thermal ageing due to the surfactant melting and re-entering the film and with light ageing through an oxidation mechanism.

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 . They were stored in dark ambient conditions and had between 14 and 22 months of natural ageing prior to testing. Prior to analysis, the films were removed from the steel plates, cut to fit the DMA clamps and preconditioned for at least 24 h in a sealed saturated salt chamber fitted with a constant flow fan, set at ~50% RH using a saturated solution of magnesium nitrate. To dry the films to <10% RH, samples were placed into glass jars containing silica gel beads, sealed and left for at least 48 h prior to testing to reach equilibrium. The samples were transferred as quickly as possible from

the humidity chamber/jars to the DMA and allowed to equilibrate within the chamber at the appropriate RH for at least 5 min prior to analysis.

Accelerated ageing

A selected group of samples were thermally aged in a Fisons 185 HWC environmental oven at 60°C and 55% RH for a period of 16 weeks. Others were light aged at 15000 lux for 16 weeks using Philips TLD 58W/840 daylight tubes with the UV component filtered by a layer of Perspex. Assuming reciprocity this is equivalent to ~50 years of exposure under museum conditions.

Instrumentation

All analysis was carried out on a Polymer Labs MkIII DMTA instrument in tensile mode, modified to include relative humidity control, described in Part 1 [6]. Experimental parameters were also described in Part 1.

Results and discussion

Response to relative humidity

Figures 1 and 2 illustrate the effect of varying RH levels on the dynamic mechanical properties of acrylic emulsion paints. Liquitex titanium white free films were thermally scanned at 10, 30, 50 and 75% RH with sample preconditioning at the corresponding RH. Choosing the 25°C point as a reference, the datum in Fig. 1 confirms that the storage modulus increased approximately ten fold with a decrease in RH from 75 to 10%, which would translate to significant shifts in tensile properties. The $\tan\delta$ curves in Fig. 2 illustrate that low RH values are reflected as low $\tan\delta$ peak heights (TDPH) and clearly illustrates the effect of test RH on the results. The TDPH increases as the polymeric structure gradually opens up with increasing levels of ambient moisture. This probably coincides with the absorption of water by hygroscopic materials within the paint such as non-ionic surfactants, which can exist in isolated pockets within the films or may be diffused into the polymer. The absorption of water into any latex film is influenced by the elasticity of the polymer, the type and amount of water-soluble materials, the polymer chemistry, the particle size of the latex, the drying conditions and

^{**} There is often a significant difference between the T_g when measured by DMA and DSC. This is due to several factors including:
 a) The heating rate/calibration – i.e. the DSC uses a small sample and the machine is thermally calibrated, whereas DMA uses a large sample and the air temperature near the sample is measured, i.e., a kinetics problem. b) The calculation method: with DSC the onset or midpoint temperature is typically measured, and if the DMA storage modulus onset temperature was used, it would lie closer to DSC values than the $\tan\delta$ peak. c) The test frequency – i.e. usually for each decade increase in frequency you typically increase T_g by 6°C.

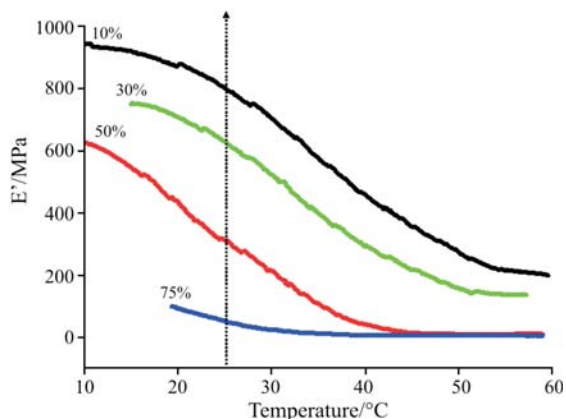


Fig. 1 Effect of preconditioning and test RH on Liquitex titanium white free films, storage modulus data (E'). Samples preconditioned to test RH in each case

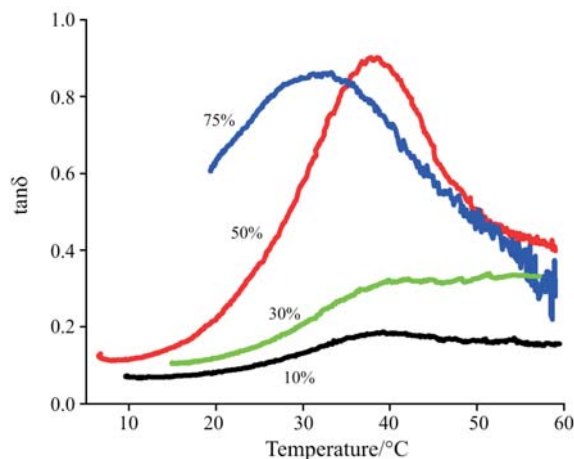


Fig. 2 Effect of preconditioning and test RH on Liquitex titanium white free films, $\tan\delta$ data. Samples preconditioned to test RH in each case

imperfections in the film. It is known that the presence of water-soluble materials and polymer polarity increases the initial absorption speed of water when compared to latexes containing less water-soluble material and of lower polarity. At RH levels above $\sim 65\%$, tests carried out by the authors confirmed that the rate of water uptake increases dramatically, which is illustrated by the 75% RH curve (Fig. 2) curve; here the $\tan\delta$ peak has shifted to the left as a result of film plasticization by the water.

Response to isothermal test temperature

A second experiment was designed to assess the effects of ambient temperature during the RH sweep. Films of Liquitex titanium white were analysed in duplicate using a humidity ramp from 10 to 80% under isothermal conditions at 10, 20 and 30 $^{\circ}\text{C}$, respectively. In addition, each temperature pair was preconditioned to either 50% RH or dryness. Figure 3 clearly illustrates

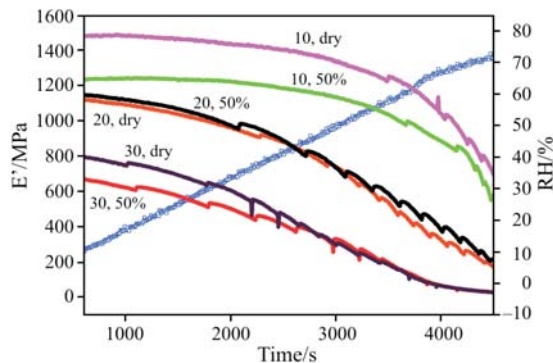


Fig. 3 Effect of different test temperatures and sample preconditioning on 10–80% humidity sweep. Liquitex titanium white free films, storage modulus data (E'). Samples preconditioned to each test RH

that modulus values are primarily influenced by test temperature. However at 10 $^{\circ}\text{C}$, the 50% RH preconditioned sample has a slightly lower modulus than the dry sample, which is due to the higher water content of the 50% sample. Preconditioning appears to have had a less pronounced effect at higher temperatures, because the paints are essentially post T_g and free moisture is being lost by the sample.

The $\tan\delta$ data for the 30 $^{\circ}\text{C}$ test in Fig. 4 illustrates that the paint has passed through its T_g , demonstrating the softening effect that occurs with moderate increases in temperature. This also shows the plasticizing effect of increasing RH on T_g , for example the 20 $^{\circ}\text{C}$ samples are pushed into the onset of the T_g region by the higher RH values. At 30 $^{\circ}\text{C}$, the RH at the T_g point is only 65%, which, although these figures are not absolute, has implications for the storage, display and transport of acrylic emulsion paintings. The combination of moderate temperatures and high RH levels will soften the paint films more quickly, making them prone to dirt pick up and increasing the possibility of surface disturbance (i.e. burnishing) from packing materials etc. during transport.

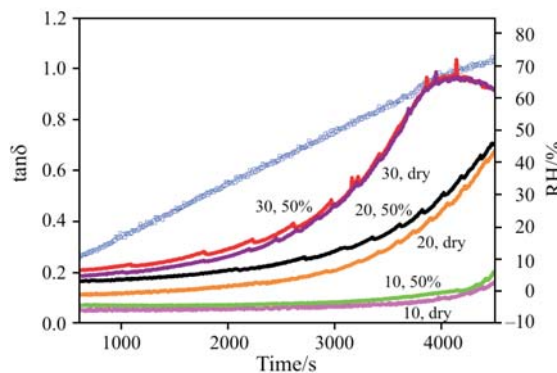


Fig. 4 Effect of different test temperatures and sample preconditioning on 10–80% humidity sweep. Liquitex titanium white free films, $\tan\delta$ data. Samples preconditioned to each test RH

Response to accelerated ageing

Figures 5 and 6 contain the results of a series of Liquitex films analysed with a humidity ramp from 10–80% RH, under isothermal conditions at $\sim 20^\circ\text{C}$. The samples included two young (18-month old) naturally aged films taken from two different draw-downs (TLNF3 and TLNF4) and some thermally aged equivalents (TLNFTH1 and TLNFTH3). Some of the samples were preconditioned to dryness ($<10\%$ RH) and others to ambient conditions at $\sim 30\%$ RH.

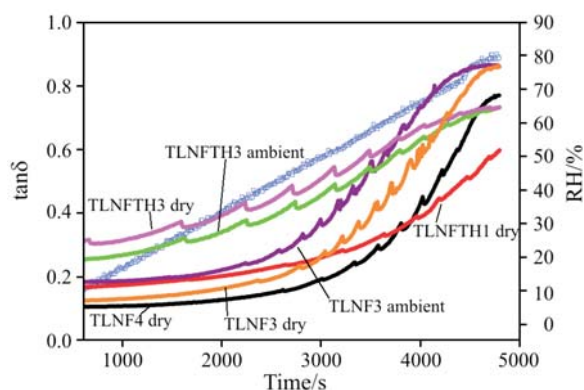


Fig. 5 Effect of different draw-downs, thermal ageing and preconditioning RH on the repeatability of various Liquitex titanium white free films, $\tan\delta$ data. Ambient= 30% RH

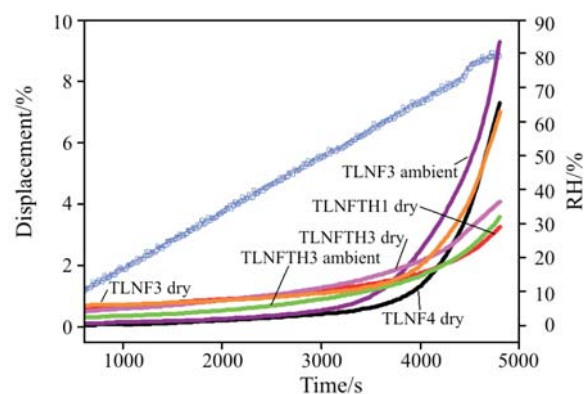


Fig. 6 Effect of different draw-downs, thermal ageing and preconditioning RH on the repeatability of various Liquitex titanium white free films, % displacement data. Ambient= 30% RH

The curves of TLNF3 ambient, TLNF3 dry and TLNF4 dry shown in Fig. 5 correspond to the young, naturally aged samples. These $\tan\delta$ curves have steeper slopes at the pre- T_g shoulder than the thermally aged samples, which may reflect differences in the moisture content of the paints. The young paints also have higher $\tan\delta$ peak values than the thermally aged samples, which may also be due to the higher moisture (and hydrophilic material) contents of the young samples. The thermally aged paints have a

shallower pre- T_g shoulder and the $\tan\delta$ values (y -axis) have decreased slightly, which probably reflects a decreased water (and hydrophilic material) content and/or more coherent particle coalescence induced by the thermal ageing regime [15]. Figure 6 includes the corresponding % displacement data for Fig. 5. It is clear that the young, naturally aged samples dried to $<10\%$ RH show a slight drop in flexibility when compared to those conditioned at 30% RH and that the thermally aged paints are less flexible.

The hydrophilic material within these paints consists, at least in part, of a nonionic surfactant (polyethylene oxide type), which was also monitored during ageing with Fourier transform infrared attenuated total reflectance (FTIR-ATR) analysis. This confirmed that the surfactant present on the surface of the films before ageing was no longer detectable after both light and thermal ageing. Despite the loss of surface surfactant however, the presence of residual surfactant within the bulk of the sample was confirmed via FTIR microscopy of 24 h water immersion extracts.

Figures 7 and 8 contain the $\tan\delta$ curves for naturally, light and thermally aged paint films of both Liquitex (Fig. 7) and Talens (Fig. 8) titanium white films. The data highlights some of the differences between these two brands, for example, the $\tan\delta$ peak values (y -axis) differ markedly, i.e., the peak heights for the naturally aged Liquitex films are ~ 0.85 and the Talens films are ~ 0.5 . This may be due to a number of factors including; the Talens samples may be more cross-linked, and/or the polymer chains may be more densely packed than in the Liquitex films. The differences may also be accounted for by copolymer chemistry, film moisture content, surfactant content (FTIR-ATR analysis showed that the Talens paints have more surfactant on the surface) and possibly the presence of the chalk (calcium carbonate) filler in the Talens samples.

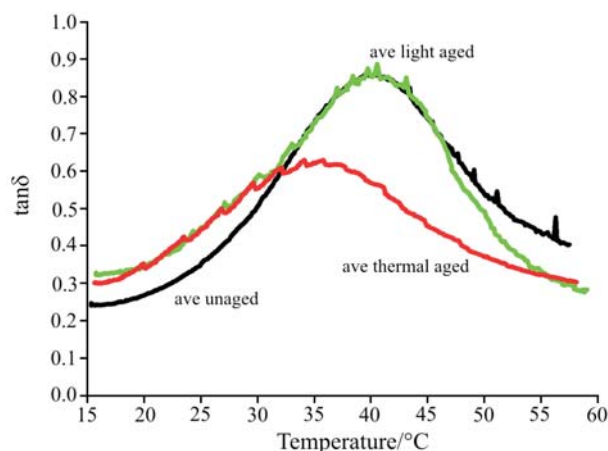


Fig. 7 Liquitex titanium white paint free films, unaged, light aged and thermally aged, $\tan\delta$ data

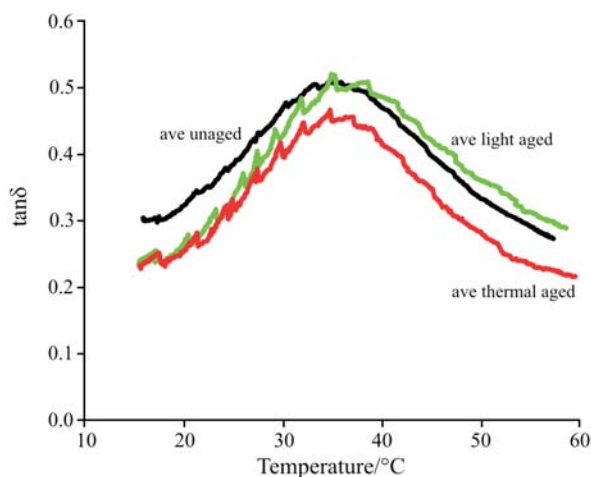


Fig. 8 Talens titanium white paint free films, unaged, light aged and thermally aged, $\tan\delta$ data

Changes induced by ageing the Talens paints were less pronounced, and for both brands, the $\tan\delta$ curves for the light aged and unaged films were essentially similar. This indicates that the loss of surfactant through light ageing does not cause any significant change to the properties of the bulk film. This is interesting as it suggests that medium to long-term display in UV free museum environments will not significantly contribute to the physical deterioration of these paints. However, the thermally aged Liquitex paint (Fig. 7) shows a significant decrease in TDPH and a drop in T_g of $\sim 7^\circ\text{C}$. The T_g decrease indicates that the physical/chemical structure of the film may have been degraded by the thermal ageing regime.

The other feature of the $\tan\delta$ curves for both brands is the zigzag effect. This is an artifact created by the DMA control and the high strain dependency of these paints. This appears to be more pronounced for the Talens paint film, possibly due to the presence of calcium carbonate filler.

Conclusions

Controlled RH DMA was successfully used to assess the properties of acrylic emulsion paints and changes occurring with accelerated ageing. Testing confirmed that these paints are: highly responsive to changes in relative humidity and temperature; that moisture plasticises the films causing a drop in T_g ; that UV free light ageing does not induce significant changes to physical properties; and that thermal ageing for prolonged periods at 60°C may contribute to polymer degradation.

It was not possible to take all aspects of the complex process of moisture sorption fully into account during testing. However it was essential that a consistent approach to controlling the moisture content of the samples was taken, including sample preconditioning

to the required test RH. In addition, to be sure that each material had equilibrated at the chosen percentage RH, every sample was conditioned prior to testing.

The Liquitex titanium white samples consistently responded more to changes in temperature, RH and ageing than the Talens paints, which may reflect differences in copolymer chemistry, surfactant content, the presence of fillers and differences in film formation etc. There is a relationship between moisture content, surfactant content and responsiveness to RH. Thermal ageing may result in degradation of the surfactant as well as increased particle coalescence, resulting in paint films that are less responsive to RH and less flexible. More encouragingly, the light aged samples, having had the equivalent exposure of approximately 50 years display in a museum environment, responded similarly to the naturally aged young films, despite the loss of surface surfactant.

The polymeric structure of the Liquitex sample may have been damaged by the thermal ageing regime, as signified by a decrease in T_g of $\sim 7^\circ\text{C}$, and requires further investigation. It would also be useful to link this information with tensile and biaxial testing data from the same paints to further establish whether the changes noted are of sufficient magnitude to significantly contribute to physical deterioration.

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; ColArt UK for providing the Liquitex paints; Talens (Holland) for providing the Talens paints; and Corus UK Ltd. for the Teflon coated steel substrates.

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Received: June 9, 2006

Accepted: July 20, 2006

OnlineFirst: February 13, 2007

DOI: 10.1007/s10973-006-7725-9