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**Film formation of artists' acrylic paints in tropical climates using dynamic speckle interferometry**

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ABSTRACT

Understanding the production of twentieth-century paintings in tropical climates is critical for the preservation of twentieth-century art produced and located in these environments.

Exploiting the characteristics of laser speckle, the research described in this contribution employs dynamic speckle interferometry (DSI) to analyse the film formation properties of three artists' acrylic paint films prepared in diverse climatic conditions. With an increased relative humidity up to 73% RH, it is shown that the rate of activity or water evaporation is decreased, there is a delayed drying time and slightly less order compared to the same films cast in ambient conditions of 50% RH. Results also indicate that DSI is able to identify differences in film thickness, brushstroke direction and the inward drying of the acrylic paint films from the edge. Such information was obtained with DSI by statistically analysing rapid variation in dynamic speckle that produces temporal data from the paint surface and calculates the time history of the speckle pattern (THSP), co-occurrence matrix (COM), inertia moment (IM) and wavelet entropy (WE).

INTRODUCTION

Vast collections of works of art produced with acrylic paints exist in tropical Southeast Asia as artists enthusiastically embraced new technological developments in paint production in the twentieth century. However this has largely occurred with a lack of understanding of the working properties and preservation issues associated with such usage. Generally though, at high temperatures and relative humidities, acrylic paints are mobile and rubbery with a low

tangent modulus as polymers are able to slide past one another and thus limit crack formation. Simultaneously, the energies obtained from higher temperatures also activate reactions and accelerate degradation processes as well as thermal expansion.<sup>1-3</sup> In the context of addressing this broader issue, this contribution investigates the film formation process of artists' acrylic paints with dynamic speckle imaging (DSI) with the aim of understanding the effects of climatic variations. According to Keddie's comprehensive report on the topic, the environmental conditions during which water evaporation and polymer coalescence occurs affect the ability of an acrylic paint film to produce closely packed structures, its levelling properties and drying times, and thus its practical application and future stability.<sup>4</sup> An investigation into the drying mechanisms of three commercial brands of artists' acrylic emulsion paint was therefore performed to assess whether this holds true with DSI analysis and ascertain whether their composition, film thickness and direction of brushstrokes had an effect on the overall drying activity of the paint film at ambient relative humidities of 50% RH and increased relative humidities up to 73% RH.

In earlier experiments undertaken by the authors, various laser speckle methods were employed to characterize cultural materials, in particular laboratory-based and *in situ* electronic speckle pattern interferometry (ESPI),<sup>5</sup> digital image correlation (DIC), laser speckle contrast imaging (LSCI)<sup>6,7</sup> and DSI. In terms of understanding the behaviour of artworks as a function of climate, although some meaningful results were obtained with ESPI, stability issues and the complexity of the optical system were problematic. Recently completed PhD research by Elaine Miles and publications by Amalvy *et al.*,<sup>8</sup> Passoni *et al.* (who also studied commercial paint drying),<sup>9</sup> and a study by Nobre *et al.*<sup>10</sup> in the biological sciences, have identified DSI as an intriguing alternative to monitor varying temporal activity. Such behaviour is common in cultural materials, for example moisture absorption of heterogeneous layered structures, sudden vibrations and environmental changes experienced during transit, and therefore in this study it was used to obtain temporal and spatial data from the surface of a paint film as it dries as a function of the surrounding climatic conditions.

## BACKGROUND

### *Film formation properties of artists' acrylic emulsion paints*

Artists' acrylic emulsion paints are synthetic, thermoplastic, copolymers of acrylate and methacrylate monomers dispersed in water with the aid of a surfactant.<sup>11</sup> These paints contain a number of additives to provide the necessary physical and chemical properties and improve

their commercial viability.<sup>12</sup>

The exact processes associated with film formation of latex paints are well researched but still uncertain, as recently outlined by Chen *et al.*<sup>13</sup> Principally, however, the drying process of acrylics can best be described in three stages: (i) evaporation of water and particle ordering; (ii) particle deformation; and (iii) interdiffusion of polymers across particle–particle boundaries, as reported by Keddie<sup>4</sup> and Learner.<sup>11</sup> Initially, the wet film is comprised of polymer particles uniformly dispersed throughout the liquid vehicle, which is followed by the evaporation of water from the paint film much like pure water behaviour<sup>14</sup> and the absorption of water into the substrate, causing the polymer particles to come together.<sup>11</sup> This is referred to as the ‘constant rate period’,<sup>8</sup> when the film exhibits its elastic, linear properties<sup>13</sup> of the viscoelastic acrylic dispersion, as noted by Hagan *et al.*<sup>15</sup> The next intermediate stage is least understood but current theories accept that further water is drawn out via a combination of mechanisms including: capillary forces as the particles come closer together;<sup>8, 16</sup> the particle volume packing model;<sup>14</sup> surface tension difference, as noted by Vanderhoff *et al.*;<sup>17</sup> and many other mechanisms described by Keddie,<sup>4</sup> such as deformation and fusion that rely on the thinning and rupturing of intermediate liquid membranes, and dry and wet sintering driven by polymer–water interfacial tension. Recent work by Chen *et al.*<sup>13</sup> also proposes three additional intermediate film formation stages between stages 1 and 2 described above. Then in the final phase, the polymer particles coalesce or interdiffuse to a point where the boundaries are hardly detectable and a continuous cohesive film is formed. A key to the stability of acrylic emulsion paints is for two adjacent polymer particles to diffuse well into one another, which occurs when the ambient temperature is greater than the glass transition temperature ( $T_g$ ) of the paint film. Generally the entire process takes upwards of 30 minutes, but this can vary from brand to brand and depends on the additives included.

In terms of the paint composition, full coalescence is dependent on the  $T_g$  and minimum film formation temperature (MFFT) of the given acrylic paint brand. Paint drying below the MFFT results in a film of high porosity as the polymer particles are too stiff to merge into one another due to its  $T_g$  at a given temperature.<sup>11</sup> Conversely paint drying above the MFFT when the  $T_g$  is greater will aid polymer particle flow and facilitate full coalescence as interstitial voids are filled.<sup>4</sup> The MFFT and  $T_g$  of an acrylic paint film can be altered according to the type of polymer, copolymer ratio and additives such as a coalescing agent, which temporarily softens the polymer particles during film formation.<sup>11</sup>

*Artists' acrylic emulsion paint, film formation and the environment*

The environmental conditions during which acrylic emulsion film formation occurs can affect its future stability. Generally, with slower coalescence greater uniformity in paint films is achieved, as the spherical polymer particles have time to deform and fill all inter-particle spaces and produce a dried film. Learner<sup>11</sup> and Lofflath *et al.*<sup>14</sup> state that it is the relative rates of water removal and the ambient conditions during drying, such as air flow, RH and temperature, which effect coalescence rates.

Temperature has been found to have a considerable effect on acrylic emulsion paint film formation. In the early stages of drying during the ‘constant rate period’ when water is evaporating from the film, the mechanism is dependent on temperature, RH, paint geometry and air flow.<sup>8, 16</sup> Vanderhoff *et al.*<sup>17</sup> showed that coalescence speeds up as heat promotes polymer particle flow. Tumosa and Mecklenburg add that the addition of heat during the drying process “may alter the coalescing of the film and even remove some of the chemical agents that induce this process”.<sup>18</sup> Hagan *et al.* also note that increased temperatures decrease the tensile curves, increase the strain failure and that the surfactant crystal melts from 35°C, which is likely to alter the equilibrium properties of the paint film.<sup>12, 15</sup> Increased RH slows down the rate of water evaporation simply because of the slower exchange of water molecules into an already saturated atmosphere and a reduction of the  $T_g$  with higher moisture contents. Acrylic paint can also respond quickly to moisture exchanges because of its dependency on  $T_g$  and the high proportion of hydrophilic constituents.<sup>3, 19, 20</sup> The increased RH and temperature that are common in tropical environments generate competing reaction pathways and it is not clear which of these dominates and controls the strain properties of a drying acrylic paint film.

A 2011 study by Chen *et al.*<sup>13</sup> using an RH of 25, 43, 60 or 75% at 25°C and a temperature of 24, 35, 45 or 55°C at 60% RH has, however, shown that high temperatures have a greater effect on film formation for a styrene/*n*-butyl acrylate copolymer compared to high relative humidities. Chen’s results show that rapid film formation occurs at the liquid–air interface at high temperatures, which causes water to be trapped between the interstices. They also identified that a high evaporation rate of water forms a less well-defined crystalline structure and uneven distribution of latex particles when there is an increase of temperature and decrease of RH. This is worth noting in tropical climates where higher temperatures and relative humidities exist. Further, in terms of the influence of pigments on the stress–strain properties of acrylic paints, Hagan *et al.* describe the influence of volume fractions of pigments and their geometry on the mechanical properties of acrylic dispersion paints.<sup>12, 15</sup> Hagan found that with an increase of pigment volume fraction, the modulus increases as the

binder is constrained and strain failure increases. In addition, the pigment geometry and associated increase in available surface area for the adsorption of water, had the greatest impact on the equilibrium moisture content of paint films.<sup>12</sup>

## THE METHOD DEVELOPED: DYNAMIC SPECKLE INTERFEROMETRY

Exploiting the characteristics of laser speckle reflecting from an optically rough surface, DSI is used to determine the relative activity of a sample by analysing dynamic speckle footage. The premise of DSI is that by recording and analysing the amplitude and frequency of fluctuations in specklegrams over time it is possible to observe and quantify the relative activity of the sample. Further, as mentioned earlier, DSI has been used previously to monitor commercial paint drying by Amalvy *et al.*<sup>8</sup> and results correlate well with conventional gravimetric methods to assess film formation. Amalvy *et al.* also showed that the ‘constant rate period’ determined by gravimetric measurements corresponded with DSI.<sup>8</sup>

{Insert Figs 1 and 2 here }

The first step in DSI analysis is the construction of an array called a time history of the speckle pattern (THSP) image, which is based on the utilization of the movement of the scattered centres. Compiled after the speckle footage has been collected with a charge-coupled device (CCD) camera, the specklegrams are stacked sequentially into a data cube formation in the x direction (yellow line, Figure 1) and y direction (purple line, Figure 1). The analysis can be performed over the entire surface, along a particular column or on a single point. If along a particular column, a THSP image can be retrieved by essentially removing slices of the cube that are parallel to the time axis and the columns are lined up parallel to one another. The upper image in Figure 2 is a THSP plot of the column through the centres in the x and y direction obtained from the drying activity of the Silpakorn University titanium white acrylic paint. Here the x axis shows the progression of time from left to right and the y axis shows the evolution of the intensity along a profile of the speckle frame. When there is high activity, the intensity will fluctuate rapidly, which results in a noisy signal progressing through time and occurs when the paint film is first cast and water evaporation is occurring, known as the ‘constant rate period.’<sup>8</sup> Provided the sampling rate of the recording device does not match the frequency of the fluctuations and the exposure rate is not equal to the period of the fluctuation, when the surface is experiencing low activity, the converse occurs and the speckle will fluctuate slowly, and the THSP will feature a continuous but ‘blurred’ line along the time axis. The arrow in Figure 2 indicates this point at 20 minutes

along the edge and at 40 minutes in the centre of the paint sample. It is at this point that activity has ceased, its ‘constant rate period’ has been reached and the paint film is considered ‘touch dry.’<sup>8</sup>

*Statistical analysis of data and theoretical premise of the algorithm*

To compare variations in acrylic paint brands, pigment types and the influence of environmental conditions on strain activity and dynamics, a THSP matrix can be further analysed with algorithms for the co-occurrence matrix (COM), inertia moment (IM), generalized difference and wavelet entropy (WE) to obtain quantitative data relating to temporal activity. Algorithms for COM and IM measure the statistical fluctuations present,<sup>8</sup> and the entropy of the system is assessed by analysing the peak frequencies of fluctuations with WE.<sup>9</sup>

The statistical method used to provide quantitative data to compare relative activity begins with the construction of the COM as defined by:

$$COM(i, j) = \frac{[N_{i, j}]}{\sum_j [N_{i, j}]} \quad (1)$$

where COM has dimensions of  $I \times I$ ,  $I$  is the maximum intensity of the THSP and  $N$  is the number of counts where a pixel has transitioned from intensity  $i$  to final intensity  $j$  in the THSP. Due to the one-dimensional normalizing effect of the denominator in equation 1, the sum of the components in each row is equal to 1. The lower image in Figure 2 plots the COM and displays the IM value for the given dataset. When there is low activity, the COM plot features a bright sharp straight line along the diagonal as the intensity has varied little between subsequent pixels. Conversely samples with high activity, as shown in the COM plot in Figure 2, have a widely spread diagonal line that plumes out due to the rapid intensity fluctuations for each pixel.

The IM is calculated by first multiplying each count value from the COM with the square of its row distance to the principal diagonal and then summing all of the values. The IM value occupies the range  $[0; \infty]$  where high values correspond to high activity and a widely spaced diagonal COM line. This is because pixels positioned at a distance further from the diagonal contribute a higher value to the IM total, which can be calculated with:

$$IM = \sum_i \sum_j COM(i, j)(i - j)^2 \quad (2)$$

With WE, entropy is a relative measure of order or disorder in a dynamical system and captures both frequency and location information. Ordered activity shows a peak in a frequency domain and its concentration of the frequency spectrum in one single peak corresponds to low entropy.<sup>9</sup> In contrast, disordered activity will show components in a wide range of frequency domains and reflect higher entropies. Wavelet transformations analysis characterizes a signal by manipulating the position and amplitude of an appropriate base wave. If the wavelet is required to form a proper orthogonal basis it has the advantage that an arbitrary function can be uniquely decomposed and the decomposition can be inverted.<sup>9</sup> In order to determine the entropy of THSP, which is a measure of the system's energy, each row running along the time axis is divided into temporal windows of length  $L$  and each segment represented by an integer  $i$  where  $i = 1, \dots, N_t$ ; with  $N_t = \text{signal length}/L$ . The mean wavelet energy of the signal is:

$$E_{i, j} = \frac{1}{N_j} \sum_{k=0}^{L/2^{j-1}} |C_{k, j, i}|^2 \quad (3)$$

where  $N_j$  is the number of wavelet coefficients,  $C_{k, j, i}$ , at resolution level  $j$  that are presented in the time interval  $i$ . The total energy of the system at interval  $i$  and its relative energy,  $p$ , are respectively:

$$E_i = \sum_{j \leq 0} E(i, j), \quad (4)$$

$$p_{i, j} = \frac{E_{i, j}}{E_i} \quad (5)$$

The value used to characterize the THSP is the Shannon entropy,  $S_i$ , which is a measure of disorder of a temporal window  $i$  and is calculated using:

$$S_i = - \sum_{j \leq 0} p_{i, j} \ln(p_{i, j}) \quad (6)$$

As this value is evaluated in a scanning window fashion, it is useful to plot images qualitatively where the dynamics of the speckle varies over the region and over time as in Figures 4 and 5.

## EXPERIMENTAL

### *Experimental bed*

The laser beams and camera were positioned so that they faced downwards, allowing the painted samples to lie horizontally while drying and to be analysed on a vibration-absorbing table. To assess the effects of climate on the samples during film formation, tests were conducted in ambient conditions of approximately 20°C and at higher RH between 65 and 73% simulated with saturated KCl salts inside a Perspex box built over the experimental bed. A T-TEC datalogger recorded the RH and temperature alongside all of the analysed samples.

{Insert Figs 3–5 here}

Figure 3 shows the experimental setup. The Photometrics SenSys 12-bit CCD camera was positioned 600 mm from the sample board with a Melles Griot HeNe 633 nm linearly polarized laser outputting a signal of 15 mW (with a single fibre output of 2.10 mW over 8 × 9 cm). The light source was coupled to a single mode optical fibre via a pigtail connection which was then coupled to a single mode, 633 nm, optical fibre 50:50 beam splitter (Oz Optics Fibre Optic Beam Splitter Coupler: 50:50, Thorlabs SM600 50:50 beam splitter). The optical fibres were then mounted onto L-mount stands to centre the expanding illuminating laser light onto the surface. The fibres were oriented such that light radiating from each end was vertically polarized.

The SenSys CCD camera was connected to a desktop computer and fitted with a 1:28, 50 mm Sigma macro lens with two additional filters including a 55 mm Nikon linear Polaroid lens and a Melles Griot narrow bandstop 633 nm filter so that the images could be acquired in ambient lighting conditions.

### *Data acquisition, interface and processing*

Full-field footage was driven by V++ software (Digital optics) and captured by the CCD camera every 20 seconds to capture 1500 dynamic images of 1034 × 1317 pixels at 250 ms exposure with codes written by one of the authors (EM: *Getexposure* and *Paintdsi*). The sample rate was determined heuristically as the dynamics of the sample are usually complex or poorly understood. The speckle footage was then analysed with the algorithms described

above with a code written by EM in MATLAB (*DSIpaintCALC*, *DSIpaintPLOT*, *WAVEpaintCALC*, *WAVEpaintPLOT*).

### *Samples*

The three commercial brands of artists' acrylic emulsion paint included Golden acrylics, Winsor & Newton Finity acrylic paints and Silpakorn University Pradit acrylics, an artists' paint manufactured in Thailand and formulated to meet the specific requirements of tropical climates. The colorants included titanium white (Rutile PW6 for the Golden and Silpakorn University paints), cadmium red (Pyrolopyrol PR254 for Golden and Silpakorn University; Pyrole PR 255 for Winsor & Newton), burnt sienna (calcined natural oxide PBr7 for the Golden; and synthetic iron oxide PR101 for the Winsor & Newton); burnt sienna was not available for the Silpakorn University Pradit acrylics. The compositional components of Golden<sup>19</sup> and Winsor & Newton<sup>3</sup> paints were obtained from the published literature and the exact proportions and material contents are known for the Silpakorn acrylic paints as one of the authors (NT) is undertaking a joint project with Associate Professor Supanee Chayabutra who formulated the paints. For commercial reasons these formulations cannot be published but the contents are comparable in material type and percent composition to the other brands, apart from an increased biocide content, the use of a Rohm and Haas binder specifically designed for tropical climates, reduced thickener and a larger coalescing aid content for the Silpakorn paints. Such compositional data provide the basis to assess their film formation properties across the brands. Furthermore, in all instances, the binder was identified as a p(*n*BA/MMA) copolymer by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometry using a Bruker instrument at CCMC.

All the films were cast on a Mylar-covered Foamcore support to minimize the influence of the substrate in the different environments and in replicate. A paint draw down bar with a clearance of 30  $\mu\text{m}$  was used to cast the films and for some samples other thicknesses were cast to assess this effect on film formation. Furthermore, for the tests undertaken at high RH, the paint tubes were acclimatized for five days prior to testing. All tests were conducted with the same experimental setup and data acquisition parameters to allow comparisons to be made across the sample group.

## EXPERIMENTAL RESULTS AND DISCUSSION

The 11 samples were analysed in ambient and increased RH conditions with THSP, COM, IM and WE calculations over the entire 1500 images. For the WE plots, a time series of 10

batches of 150 images was analysed, which corresponds to a time interval of five minutes for each plot, as shown in Figures 4 and 5. Figure 2 shows an example of the THSP and COM plots and IM values obtained for the Silpakorn University titanium white acrylic formed in ambient conditions of 19.5°C and 50% RH. From the THSP image it is possible to estimate the time at which the paint ceases activity, when regular lines appear to indicate that the paint film is ‘touch dry.’ It can be seen that activity ceases closer to the edge at 20 minutes compared to the centre at 40 minutes, as indicated by the purple arrow. This graduated change between these two points shows that the outer edges dry faster than the centre. The non-uniform drying nature of paint films can also be observed by looking at intensity signals at higher or lower points along the vertical axis where the noisy signal is seen to stabilize sooner (from 20 minutes onwards).

When comparing results for the same sample cast at 73% RH and 19.5°C, low activity in the THSP image appears much later (at 40 minutes) inferring that there is a much longer constant rate period and the COM plot is thinner and closer to the principal diagonal, as the intensity has varied little between subsequent pixels. Further the  $IM_y$  is 88,712 and  $IM_x$  97,513 compared to the higher and more active  $IM_y$  213,762 and  $IM_x$  312,894 obtained at lower RH. This decrease of activity with increased RH was observed for all the samples highlighting their hydrophilic behaviour and slower evaporation rate, although a limitation of this experimental setup was the reduced air flow in the environmental chamber, which was also likely to have contributed to this result. Overall, this trend supports the view that increased RH reduces the temporal activity associated with paint film formation due to there being more water vapour in the air and a slower exchange or evaporation rate with the surface of the paint layer. In addition, the plasticization of the polymer and thus reduction of its  $T_g$  would reduce polymer activity and possibly lower the MFFT as described by Keddie<sup>4</sup> and Hagan.<sup>15</sup> At higher RH, such a decrease in activity, evaporation rates and a slowing down of paint coalescence during film formation, is confirmed by Chen *et al.*<sup>13</sup> and Keddie,<sup>4</sup> who also show that a more tightly packed and crystalline structure is formed under these conditions. Chen investigated film formation of latex paints with synchrotron radiation small-angle X-ray scattering (SAXS) and found that at lower RH and high temperatures (above 35°C) “lattice faults [appear] during film formation” and a “less defined crystalline structure”.<sup>13</sup> Furthermore, the relative distribution of latex particles in a dried film, determined by the Peclet number (PE), was uniform for films formed at 75% RH/25°C and 60% RH/14°C compared to the aggregation of latex particles at the air–surface interface at higher temperatures. Thus film formation at an increased RH of 75% is appropriate provided

the temperatures are less than 35°C. This data provides firm foundations for future evaluations of the mechanical stability of the paint films with DSI.

{Insert Table 1 here}

Table 1 includes a summary of the IM values obtained from the samples analysed to compare the temporal activity of the paint brands and casting methods. Of note is that the increased wet film thickness of 70 µm for the Silpakorn titanium white film reduced the activity and ‘touch dry’ time as shown by the THSP plots that were recorded and the decreased IM values. In addition, the SuTiWhite wire samples tested in duplicate have significantly different  $IM_x$  values of 50,841 and  $IM_y$  value of 27,796, highlighting lower activity in the y direction. This corresponds to the manner in which the paint was cast, which aimed to simulate impasto brushstrokes with differential paint thickness. As the paint was applied parallel to the y axis, such lower activity is linked to the drying time of the thinner area of paint at the low points of the simulated impasto paint. Further, across the brands, the Winsor & Newton and Golden acrylic IM values were comparable for the titanium white and burnt sienna films, but the IM values for the Silpakorn University paints were significantly larger, indicating a faster rate of speckle fluctuations and greater activity over the same time period. Given that the composition of the paints is known, this is likely to relate to the reduced thickener content (by 1/24) for the Silpakorn University paint compared to the other brands and thus availability of water to freely evaporate and the incorporation of higher coalescent agent content.

Another issue relates to the effect of pigment type on film formation. The THSP plots and IM values for the Golden acrylic paints showed a clear distinction between the pigments. In order of high to low activity (together with the quickest to slowest ‘touch dry’ times) they ranked titanium white, cadmium red and then burnt sienna. This corresponds with the known behaviour of these pigments and their critical volume pigment concentration, as an increase in volume fraction for the titanium white paint increases the modulus and thus drying time.<sup>15</sup> Furthermore, Hagan’s discussion on the geometry and size of particles is another area worthy of assessment in regard to the pigmented paint films in this study.<sup>12</sup> However, the Winsor & Newton and Silpakorn University brands did not follow the same trend and this requires much further investigation. This latter result was also noted in studies by Amalvy *et al.*<sup>8</sup> and Keddie,<sup>4</sup> in which it was observed that the evaporation process at the surface is affected very little by the components of the paint (binder and pigments), although this is not the view of Hagan.<sup>12</sup>

To assess the non-uniform film formation characteristics of the acrylic emulsion

paints, the WE results presented in Figures 4 and 5 show the differential degree of order and disorder of the Golden acrylic titanium white paint film in ambient conditions of 20°C, 47–50% RH compared to the higher RH of 65–73% at 19°C. Worth noting is that over time the radius of the ‘high activity’ region, as indicated by the large negative entropy values, decreases until all of the pixels have a value near zero at 50 minutes. The figures also show the full-field wavelet entropy for different time intervals of five minutes up to 50 minutes. In the first four intervals to 20 minutes, WE values are relatively constant and then fall within the ‘constant rate period’ described by Amalvy *et al.*<sup>8</sup> and relate to a greater degree of order. From 20 minutes, Figures 4 and 5 show higher entropy values and levels of disorder, indicating the non-uniform drying activity and the viscoelastic properties of acrylic paint dispersions, as detailed by Hagan.<sup>20</sup>

## CONCLUSIONS

This study has shown that DSI is able to distinguish non-uniform and temporal activity from the surface of an artists’ acrylic emulsion paint as it dries and as a function of the surrounding climatic conditions. With an increase in RH there is a decrease in activity, highlighting the paint’s hydrophilic behaviour, and thus a decreased relative rate of water evaporation – indicated by the higher IM values and delayed drying times shown with the THSP plots. The WE plots also confirmed a lesser degree of entropy or disorder in the first stages of drying within a 20-minute time frame, which corresponds to the ‘constant rate period’, then greater WE at the later stages of drying. Such results are consistent with the literature and the non-uniform behaviour of acrylic dispersions. With the slower water evaporation during film formation at higher RH, acrylic paint films are able to produce more closely packed and crystalline structures, which may have future stability implications. The recent study by Chen *et al.*,<sup>13</sup> however, identified optimum film formation conditions at 14°C and 60% RH, but also noted that higher relative humidities were favourable and found that high temperatures were the most problematic. This, together with the results presented in this paper, will be of interest for further studies on the mechanical response of paint films. Results also indicate that DSI is able to identify differences in film thickness, brushstroke direction and the inward drying of the acrylic paint films from the edge. A limitation of this study, however, has been the use of the environmental chamber to simulate higher RH conditions, which reduced the airflow during film formation.

Importantly, DSI has been shown to be a useful tool to demonstrate non-uniform

variations in surface activity by recording and analysing the amplitude and frequency of fluctuations in specklegrams over time with time history speckle pattern, co-occurrence matrix, inertia moment and wavelet entropy calculations. DSI also overcomes the stability issues that occur with other laser speckle methods to assess displacement and can operate in real time and non-invasively, which offers many advantages in the area of materials' conservation.

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## REFERENCES

1. Michalski, S., 'Paintings: their response to temperature, relative humidity, shock and vibration', in *Art in Transit: Studies in the Transport of Art*, ed. M. Mecklenburg, National Gallery of Art, Washington (1991) 223–241.
2. Hagan, E., Charalambides, M., Learner, T., Murray, A. and Young, C., 'Factors affecting the mechanical properties of modern paints', in *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. Krueger and M. Schilling, Getty Conservation Institute, Los Angeles (2007) 227–235.
3. Ormsby, B., Hagen, E., Smithen, P. and Learner, T., 'Comparing contemporary titanium white based acrylic emulsion grounds and paints: characterisation, properties and conservation', in *Preparation for Painting: The Artist's Choice and its Consequences*, ed. J. Townsend, T. Doherty, G. Heydenreich and J. Ridge, Archetype Publications, London (2008) 163–171.

4. Keddie, J., 'Film formation of latex,' *Materials Science and Engineering Reports* **21**(3) (1997) 101–170.
5. Tse, N., Roberts, A. and Sloggett, R., 'A preliminary understanding of oil paintings in tropical Southeast Asia', in *ICOM Committee for Conservation, 15th Triennial Conference, New Delhi*, ed. J. Bridgeland, Allied Publishers, New Delhi (2008), vol. II 641–650.
6. Miles, E., Roberts, A., Sloggett, R. and Tse, N., 'Speckle and conservation', in *9th International Conference on NDT of Art*, ed. A. Notea, International Seminars, Jerusalem (2009) 1–9.
7. Miles, E. and Roberts, A., 'Non-destructive speckle imaging of subsurface detail in paper-based cultural materials', *Optics Express* **17** (2009) 12309–12314.
8. Amalvy, J., Lasquibar, C.A., Arizaga, R., Rabal, H. and Trivi, M., 'Application of dynamic speckle interferometry to the drying of coatings', *Progress in Organic Coatings* **42** (2001) 89–99.
9. Passoni, I., Dai Pra, A., Rabal, H., Trivi, M. and Arizaga, R., 'Dynamic speckle processing using wavelets based entropy', *Optics Communication* **246** (2005) 219–228.
10. Nobre, C., Braga, R.A., Costa, A., Cardoso, R., da Silva, W. and Safadi, T., 'Biospeckle laser spectral analysis under inertia moment, entropy and cross-spectrum methods', *Optics Communication* **282** (2009) 2236–2242.
11. Learner, T., *Research in Conservation: Analysis of Modern Paints*, J. Paul Getty Trust, Los Angeles (2004).
12. Hagan, E., Charalambides, M., Young, C., Learner, T. and Hackney, S., 'Influence of the inorganic concentration and geometry on the viscoelastic properties of latex coatings', *Polymer* **52** (2011) 1662–1673.
13. Chen, K., Fisher, S. and Men, Y., 'Temperature and relative humidity dependency of film formation of polymeric latex dispersions', *Langmuir* **27** (2001) 12807–12814.
14. Lofflath, F. and Gebhard, M., 'Rheological changes during the drying of a waterborne latex coating', *Journal of Coatings Technology* **69** (1997) 55–66.
15. Hagan, E., Charalambides, M., Young, C., Learner, T. and Hackney, S., 'Tensile properties of latex paint films with TiO<sub>2</sub>', *Mechanics of Time-Dependent Materials* **13** (2009) 149–161.
16. Brown, B., 'Formation of films from polymer dispersion', *Journal of Polymer Science* **XXII** (1956) 423–434.
17. Vanderhoff, J., Bradford, E. and Carrington, W., 'The transport of water through latex

- films', *Journal of Polymer Science: Polymer Symposia* **41** (1973) 155–174.
18. Tumosa, C. and Mecklenburg, M., 'Weight changes in acrylic emulsion paints and the implications for accelerated aging', *Western Association for Art Conservation (WAAC) Newsletter* **25**(3) (2003) 12–14.
19. Erlebacher, J.D., Brown, E., Mecklenburg, M.F. and Tumosa, C.S., 'The effects of temperature and relative humidity on mechanical properties of modern painting materials', in *Materials Issues in Art and Archaeology III*, ed. P.B. Vandiver, J.R. Druzik, G.S. Wheeler and I.C. Freestone, Materials Research Society, Pittsburgh **267** (1992) 359–370.
20. Hagan, E. and Murray, A., 'Effects of water exposure on the mechanical properties of early artists' acrylic paints' in *Materials Issues in Art and Archaeology VII*, ed. J. Mass, J. Merkel, A. Murray and P. Vandiver, Materials Research Society, Pittsburgh **852** (2005) 41–47.

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