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FRONT COVER

Raphael, *An Allegory* ('*Vision of a Knight*') (NG 213),
detail of PLATE 13, page 16.

TITLE PAGE

Nicolas Lancret, *The Four Times of Day: Morning*
(NG 5867), detail of PLATE 1, page 49.

A note on the reproductions

The reproductions of complete paintings from the National Gallery's collection in this book have been printed from colour-correct, high-resolution digital scans made with the MARC II Camera. This process was described in 'The MARC II Camera and the Scanning Initiative at the National Gallery', *National Gallery Technical Bulletin*, 23, 2002, pp. 76–82.

Infrared examinations were performed by Rachel Billinge, Rausing Research Associate in the Conservation Department. Infrared reflectography was carried out using a Hamamatsu C2400 camera with an N2606 series infrared vidicon tube. The camera is fitted with a 36mm lens to which a Kodak 87A Wratten filter has been attached to exclude visible light. The infrared reflectogram mosaics were assembled using Vips-ip software.

For further information about the software see the Vips website at www.vips.ecs.soton.ac.uk

The Effect of Relative Humidity on Artists' Pigments

DAVID SAUNDERS AND JO KIRBY

THE IDEAL PIGMENT IS INERT: it does not react with other components in the paint layer within which it is dispersed and is stable to the effects of light, moisture, temperature and other factors in its environment, for example pollutant gases or biological action. In practice this counsel of perfection is rarely reached but is approached by, for example, iron oxide pigments, carbon black and some modern pigments. For most of the materials used as pigments, the conditions under which they are unsuitable became well known to artists and they made their choice or adjusted the method of application accordingly. Pigments sensitive to alkaline environments, for example, were not recommended for use in a lime-containing plaster in *buon fresco*,¹ but could be applied bound in another medium after the plaster had dried. In later centuries, however, changing environmental conditions, changes of taste, or simply the passage of time may well have caused discoloration or other alterations to the pigments, in spite of the care taken by the original painter.

In many reports of pigment change in humid conditions, it is clear that the binding medium used may have a considerable influence. Drying oils are not miscible with water; the pigment particles are coated with the oil during grinding and after drying the resultant paint film is coherent and relatively impervious to moisture. Egg tempera films are quite resilient when dry, but the pigment may be less well bound, so less well protected. Animal skin glue or gum paint films usually have a more open structure with less well-protected particles in a medium that retains the ability to take up or lose moisture. Under these conditions, and in any lean paint film (as in a traditional watercolour), the pigment is more vulnerable to damage from environmental factors such as high humidity.

Occurrences of pigment change

Certain pigments appear to be particularly vulnerable to damp conditions. They include the lead-contain-

ing pigments lead white and red lead, blue basic copper carbonate – azurite – and red mercuric sulphide (α -HgS), vermilion. Red lead or minium (lead(II, IV) oxide, Pb_3O_4) is particularly interesting in this respect as both darkening and lightening of the pigment have been noted.² Darkening of red lead to brown or black lead dioxide (lead(IV) oxide) has been reported on wall paintings and also occasionally in manuscripts and prints. A principal agent appears to be light and the pigment is particularly vulnerable in an aqueous binding medium.³ Examples of darkening include the nave paintings of about 1275 in the church of Gundsømagle in North Zealand, Denmark.⁴ Humidity is suggested as one factor in the change, but high pH and microbial activity may also play a part.⁵ The ninth-century Carolingian wall paintings at the Müstair Convent in south-east Switzerland have suffered from rising damp and salt migration and here also red lead was found to have darkened to lead dioxide.⁶ Red lead in an animal skin glue medium has traditionally been used on wooden buildings in Japan for many centuries and darkening, caused by light exposure and humidity, is well known. Other environmental factors may be of importance: for example, in the Itsukushima shrine at Miyajima-cho, Hiroshima Prefecture, which is on the sea front, high salinity may play a part.⁷

Lightening of red lead has been less frequently mentioned. Its transformation to basic lead carbonate (lead white, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), by the action of carbon dioxide and moisture, has been described on Japanese sliding doors, screens, and panel paintings in an animal skin glue medium.⁸ In the early twelfth-century wall paintings in the apse of St Gabriel's Chapel, Canterbury Cathedral, areas of red lead-containing paint were covered with a veil of cerussite (lead carbonate, PbCO_3 ; identified by X-ray diffraction).⁹ Moisture and light were thought to have contributed to this change. Red lead is often less vulnerable in easel paintings, even in an egg tempera medium.

Vermilion tends to darken to what is thought to

be a form of the black metacinnabar (α -HgS), although the layer of deterioration product formed on the paint surface is so thin that conventional methods of instrumental analysis have been ineffective. The deterioration is often patchy and poorly bound pigment is more prone to alteration.¹⁰ The colour change of the pigment is not straightforward, but light, trituration, humidity and the presence of impurities (in particular alkali metal halides) have all been implicated in the deterioration process.¹¹ There are many examples of darkened vermilion in wall paintings, such as the thirteenth-century scheme in the vault of the Holy Sepulchre Chapel, Winchester Cathedral,¹² and the fragmentary early fifteenth-century paintings in the chapel of Farleigh Hungerford Castle, Somerset.¹³ The phenomenon is also common on easel paintings,¹⁴ although here the role of atmospheric moisture is rather more subtle and less easy to assess. Vermilion synthesised by the wet process¹⁵ is more vulnerable than either the dry process pigment or the natural mineral cinnabar, partly due to impurities, particularly thiosulphate salts, present in the digestion liquor.¹⁶ The presence of chloride ions in mineral cinnabar, or exposure of pure vermilion to halides, causes them to become photosensitive and to darken on exposure to light.¹⁷ In addition, the darkening can be accompanied by the formation of white mercury(I) chloride, which can result in the paint appearing grey or lilac, rather than black.¹⁸ As chloride is implicated in the change it is not surprising that greyish vermilion has been observed on artefacts in seaside environments.¹⁹

The transformation of blue azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) to a green compound has frequently been observed in wall paintings. An often-quoted example is the colour change in the cycle of the legend of Saint Francis in the Upper Church of St Francis at Assisi.²⁰ Other examples include the wall paintings at Gundsømagle, mentioned above,²¹ and the early twelfth-century scheme in St Mary's church, Kempsey, Gloucestershire.²² Although the product of alteration has sometimes been thought to be the closely related basic copper carbonate, malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$),²³ this has not been confirmed analytically. Chlorine-rich alteration products have been identified quite frequently, including at Gundsømagle, in the decorative scheme of the Ante-Reliquary Chapel, Norwich Cathedral (c.1300), and in the fourteenth-century Apocalypse cycle in the chapter house of Westminster Abbey.²⁴ The alteration products include paratacamite (rhombohedral $\text{Cu}_2(\text{OH})_3\text{Cl}$), identified in the wall

painting of San Antonio Abate in the church of San Pietro, Quaracchi, near Florence,²⁵ and atacamite (orthorhombic $\text{Cu}_2(\text{OH})_3\text{Cl}$), identified as an alteration product on synthetic azurite in frescoes in the seventeenth-century church of the Apostle John in the Rostov kremlin.²⁶ Green copper salts of this type need not necessarily be alteration products at all, but could have been used in the original scheme:²⁷ this cannot be entirely ruled out at Gundsømagle, for example.²⁸ These chlorides may also derive from alterations of other copper green pigments such as verdigris.²⁹

Conversion of azurite to tenorite, black copper(II) oxide (CuO), has been reported less frequently. A black surface alteration product, identified as tenorite, was found on fragments of late Gothic sandstone sculptures at Bern Minster, Switzerland, which had been buried in 1528. The moist alkaline conditions of the burial site, where lime was also present, are thought to have caused the conversion.³⁰

Other pigments, such as lead white, orpiment, Prussian blue, and red and yellow lakes, are well known to deteriorate under the influence of light or particular environmental conditions and here moisture may play a part. Prussian blue is known to be sensitive to alkaline conditions, even to the extent that watercolour paintings displayed on a freshly plastered – therefore slightly damp and alkaline – wall were observed to change colour.³¹ The relationship between the light sensitivity of Prussian blue and the relative humidity (RH) of the environment, without the additional factor of alkalinity, is not known, however.

Where high humidity is implicated in colour change, it is difficult to dissociate the effects of moisture from those changes caused by certain ions in solution, for example chloride ions as described above. However, simple changes in pH may also be important. Brown 'malachite staining' on a seventeenth-century votive tablet in the Kiyomizu-dera Temple, Kyoto, was found to result from deterioration of a size containing animal skin glue and aluminium potassium sulphate. Hydrolysis of the alum in high humidity appeared to have produced sulphuric acid which reacted with the glue, causing the stains.³² Because the effects of the colour changes are often very disfiguring, ruining the original aesthetic intention, attempts have sometimes been made to convert the alteration product into another compound of the same colour as the original pigment, but with varying success.³³

TABLE 1 Pigments and media used

PIGMENT	MEDIUM	MODIFICATION
No pigment	linseed oil	
Azurite	acrylic; casein; glue; linseed oil; watercolour	
Azurite	casein	painted over lime
Azurite	glue	mixed with lime
Azurite	glue; linseed oil	mixed with salt
Brazilwood lake *	linseed oil; watercolour	
Buckthorn lake *	linseed oil; watercolour	
Chrome yellow	linseed oil	
Cochineal †	dyed on silk	
Kermes †	dyed on silk	
Lac lake *	linseed oil; watercolour	
Lead(II) oxide	linseed oil	
Lead white	linseed oil; tempera; watercolour	
Lead-tin yellow type I	linseed oil; tempera	
Lead-tin yellow type II	linseed oil	
Malachite	linseed oil; watercolour	
Naples yellow	linseed oil	
Orpiment	linseed oil; watercolour	
Prussian blue (SC) ‡	linseed oil; watercolour	
Prussian blue (ALP) ‡	watercolour	
Red lead	acrylic; casein; tempera; watercolour	
Red lead	casein	mixed with lime
Smalt	linseed oil	
Ultramarine	linseed oil; tempera	
Verdigris	linseed oil; watercolour	
Vermilion	linseed oil; tempera	dry process
Vermilion	linseed oil; tempera	wet process
Vermilion	watercolour	

* The preparation of the lake pigments is described in an earlier article.⁴¹

† Both silks were dyed using the method given for the cochineal sample in an earlier article.⁴²

‡ See TABLE 1 pp. 92–3 in this *Bulletin* for a key to Prussian blue samples.

Previous studies

The effects of changes in RH on the different supports used for paintings – wood, paper, fabrics, plasters and mortars on a wall – are well known and have been widely studied. In wall paintings, problems are caused not only by atmospheric moisture and condensation on the surface as a result of temperature change, but also by movement of water within the wall, bringing dissolved salts to the painting. Attempts to control damage to the building by excess moisture have not always been entirely beneficial to wall paintings.

Moisture may cause severe damage to easel paintings, such as warping of a panel support or separation of the entire paint film from the support, but this is generally the result of repeated cycling of RH, a long exposure to increased humidity, or a catastrophic event, such as flooding. The more

subtle, long-term effects observed in wall paintings, which result from the continual presence and movement of water and salts in the wall structure, do not usually occur in easel paintings.

There has been some interest in the possible effect of high moisture levels on the light-induced deterioration of certain pigments. However, there are only a few systematic studies into the effect of RH on artists' pigments, and these tend to concentrate on the one or two materials found in the paintings that prompted the investigation. These include the effect on the basic copper carbonate pigments azurite and malachite,³⁴ vermilion,³⁵ and lead-based pigments.³⁶ In addition a number of studies have been made of the effect of RH on fading of dyed fabrics, which have indicated that the higher the RH, the greater the degree of colour change for a given light exposure.³⁷

Three studies of the behaviour of a number of

pigments have been conducted. Kühn examined the rate of fading of the organic colorants magenta, archil (orchil), brazilwood, saffron, ripe and unripe Persian berries (buckthorn) bound in gum medium and painted out on paper.³⁸ The samples were irradiated at 25, 45 or 65% RH. Increased RH accelerated the rate of fading (three to four times for an increase from 25 to 65% RH).

Bailie and co-workers considered the behaviour of four pigments (carmine lake, gamboge, alizarin lake and Vandyke brown) painted out with titanium white in PVA (polyvinylacetate) medium at relative humidities between 5 and 80%.³⁹ The rate of fading of gamboge was essentially unaffected by RH, while carmine lake and Vandyke brown showed a two- to three-fold increase in the rate of fading. Most influenced by RH was alizarin lake, which faded more than five times faster at 80% than at 5% RH. For the carmine lake the rate of fading was higher when painted out in more hydrophilic media; the rate was again highest at 80% RH.

Finally, in a previous study, the authors subjected a number of materials, including cochineal-dyed silk, cochineal, lac and buckthorn lakes, and indigo, all of which are known to be affected by light, to exposure at three different relative humidities.⁴⁰ It was concluded that increased RH, at a constant temperature, caused a greater colour change in every case.

Experimental studies

A series of experiments was conducted to examine the effect of RH on light-induced colour change in artists' pigments. The range of materials studied included those that, according to the literature, are affected by moisture, along with other pigments also commonly found in easel paintings. In most cases, the pigments were bound in both a hydrophobic (linseed oil) and a hydrophilic (gum or glue) medium, to assess the role of the binder in protecting the pigment from moisture. Details of the pigments and media are summarised in TABLE I.

Several methods are available for maintaining RH in sealed enclosures, including saturated solutions of different salts and solutions containing different percentages of sulphuric acid or glycerol.⁴³ Saturated salt solutions were used in these studies. The often-reported drawback of using saturated solutions is salt creep, the recrystallisation of the salts further up the sides of the vessel containing the solution and, ultimately, elsewhere in the chamber, at worst on the samples themselves.⁴⁴ To combat

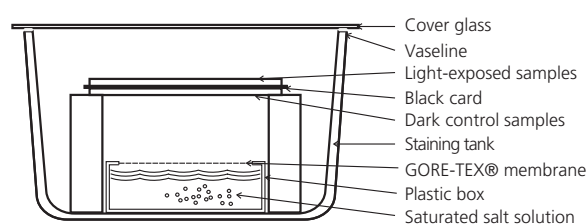


FIG. 1 Experimental set-up for the glass tank used for the first two studies.

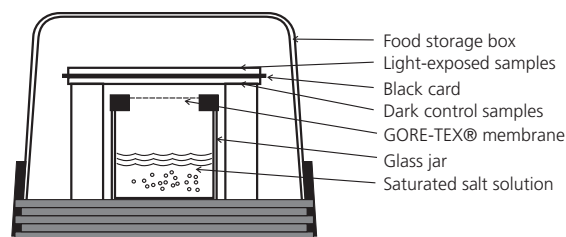


FIG. 2 Experimental set-up for the plastic box used for subsequent studies.

this problem the saturated salt solutions were contained in plastic boxes or jars which were closed using a GORE-TEX® membrane that allowed free passage of water vapour while preventing salt creep. The method used was similar to that employed by Creahan to control the RH in a display case.⁴⁵

Five relative humidities were chosen to represent the range of environments that might be encountered by paintings. Condensing (~100% RH) or moisture-free (~0% RH) conditions were not examined, as the effects expected from contact with liquid water might be rather different. Five salts, lithium chloride, magnesium chloride, magnesium nitrate, sodium chloride and barium chloride, provided the different conditions. At $24.5 \pm 1^\circ\text{C}$, these gave measured relative humidities of approximately 11% [LiCl], 32% [MgCl₂], 51% [Mg(NO₃)₂], 75% [NaCl] and 90% [BaCl₂].

For the initial experiments, the samples were held in glass staining tanks sealed with a glass plate using petroleum jelly (Vaseline); see FIG. 1. This set-up was not without problems, as on each occasion that the tank was opened to make colour measurements the Vaseline had to be cleaned off thoroughly to avoid contaminating the samples, and new Vaseline applied. As the fading chamber was slightly warmer than ambient, some batches of Vaseline tended to run down the tank walls. These batches were found to have slightly lower melting points than African-manufactured Vaseline which was used subsequently.⁴⁶ For later experiments sealable polymeric boxes, designed for airtight food storage, were

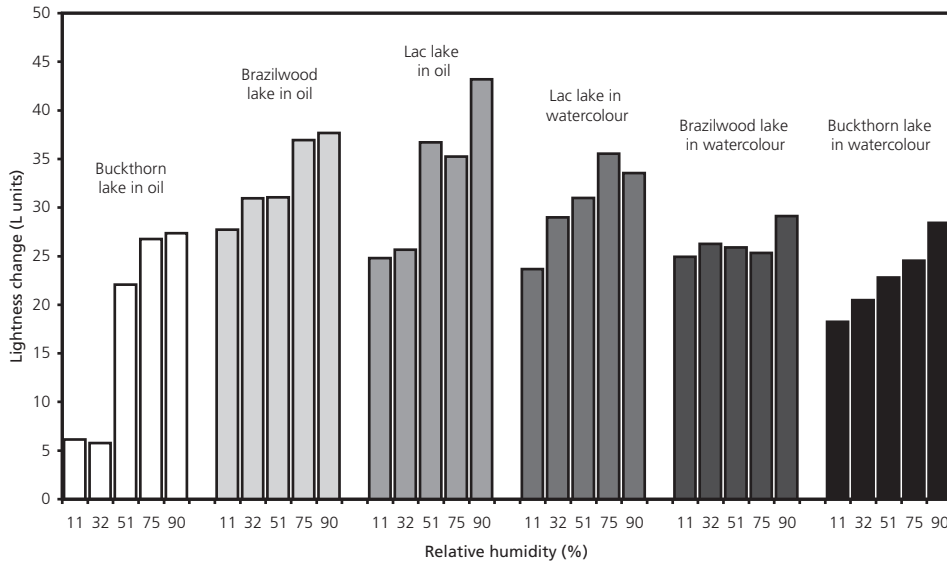


FIG. 3 Light-induced colour change for lake pigments exposed to light for ~70 Mlux.h at different relative humidities.

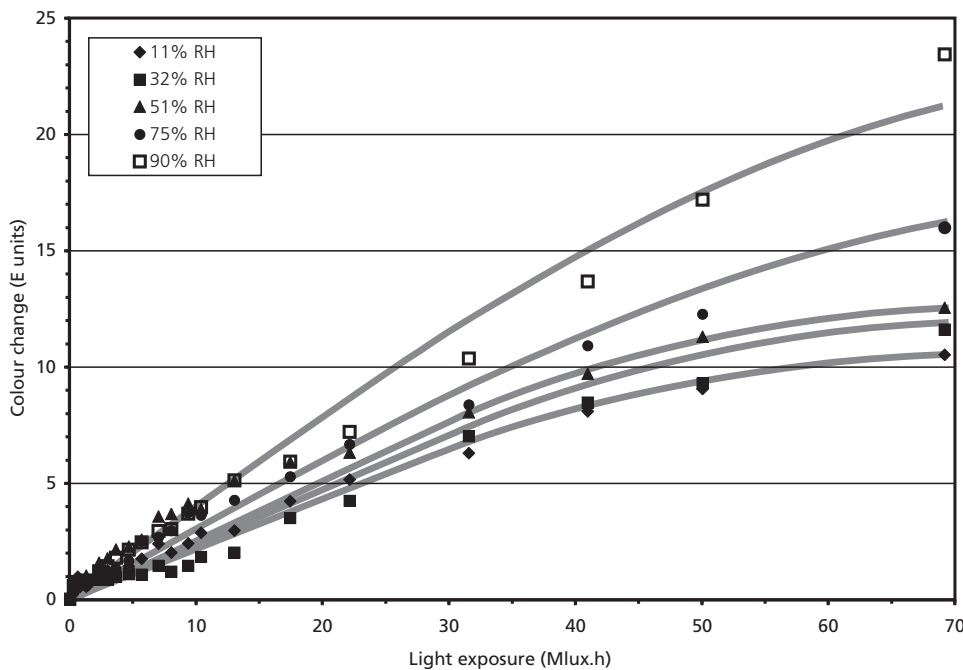


FIG. 4 Light-induced colour change for kermes-dyed silk at different relative humidities.

adopted, see FIG. 2. Before the experiments commenced, a data logger was placed in the enclosures to establish how quickly the environment reached equilibrium when the appropriate saturated salt solution was introduced, and to confirm that the chamber maintained this RH over time.

The light-ageing equipment has been described previously.⁴⁷ The samples were exposed in a light box equipped with twelve 65W General Electric *Artificial Daylight* lamps, giving an illuminance of up to 22,000 lux. The temperature in the light box during the period of these experiments was either $27 \pm 3^\circ\text{C}$ or $24 \pm 2^\circ\text{C}$. The dark control samples for each experiment were placed beneath opaque black

card in the same enclosures as the light-exposed samples, and were, therefore, maintained at the same RH.

Colour measurements were conducted with either a Minolta CR200 or CR221 chroma meter; the use of both meters has been described previously.⁴⁸ The data were converted to Commission Internationale de l'Éclairage (CIE) L^* , a^* , b^* coordinates using the standard illuminant D65 as reference.⁴⁹ Colour changes in the samples were expressed either as overall colour change (ΔE , calculated using the CIE 1994 formula),⁵⁰ or as a change in lightness ΔL . The measurements reported in FIGS 3 and 4 have an error of approximately ΔE

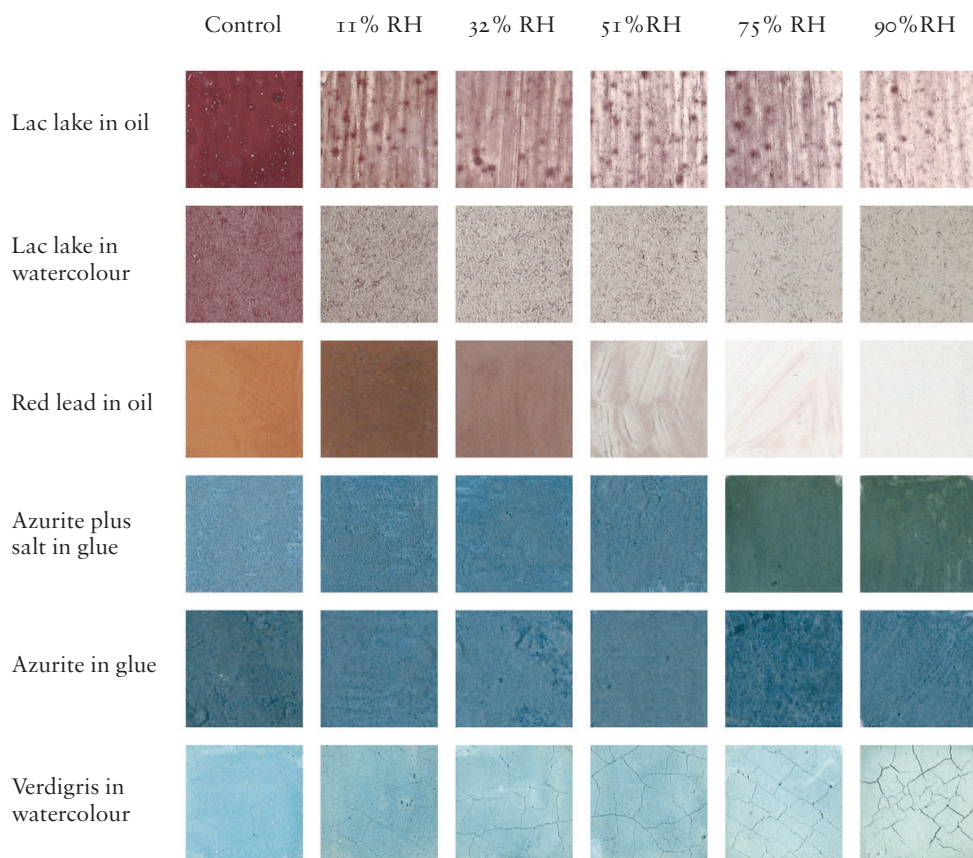


PLATE 1 The effects of RH on light-induced colour change. The control samples illustrated had been kept in the dark at 11% RH.

± 2 ; $\Delta L \pm 1.0$. A Minolta CM-2600d spectrophotometer was used to record spectra for some samples (FIGS 5 and 6).

Results and discussion

The materials studied (see TABLE 1) fall into four broad, if slightly overlapping, categories in terms of their behaviour towards light at different relative humidities. The first group consists of those that are largely unaffected by light regardless of RH. In this category are lead white, Naples yellow and malachite in any of the media studied. Most of the samples of azurite were similarly unaffected, including samples bound in linseed oil, acrylic, casein, glue, and a layer of azurite bound in casein applied over lime to mimic the stratigraphy of certain wall paintings. Even a sample of azurite to which some lime was added before binding in glue remained unaffected at all the relative humidities. Although, in common with many types of Prussian blue,⁵¹ the samples of this pigment turned slightly grey on exposure to light, there was no obvious dependency on the RH at which exposure occurred.

The second group of pigments comprises those that showed a greater degree of light-induced colour

change as the RH increased; these materials were unaffected in the dark. They include the lake pigments, the dyed silks and vermilion.

FIG. 3 shows the degree of fading at different relative humidities for the lake pigments in oil and watercolour media, demonstrating the general trend towards greater fading as RH increases. As the thin washes of watercolour were lighter at the beginning of the experiment, the overall lightness changes were greater for the samples bound in oil. After exposure the oil-bound samples were markedly better preserved than the equivalent watercolour samples (PLATE 1).

The samples of kermes- and cochineal-dyed silks behaved as might be expected from previous reports.⁵² As RH increased, the degree of fading of the dyestuff also increased; see FIG. 4.

The four types of vermilion showed similar behaviour, with the greatest darkening at high RH. FIG. 5 shows reflectance spectra for oil-bound wet process vermilion after light exposure. The greater degree of darkening is evident in the reduced reflectance at the red end of the spectrum, particularly in the sample maintained at 90% RH. It was also noticeable that the wet process samples darkened more than the dry process samples bound in

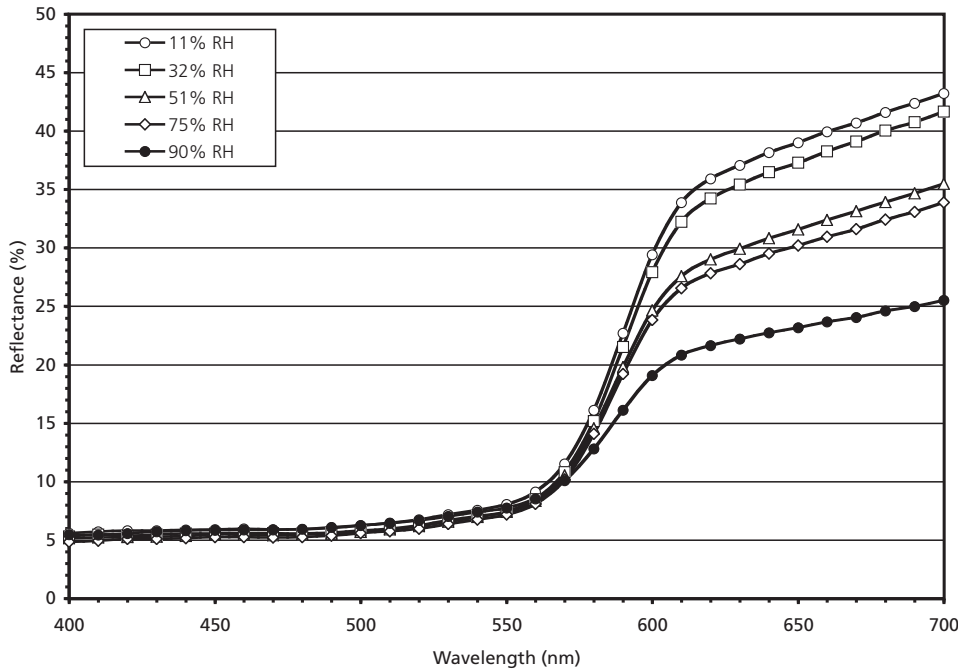


FIG. 5 Reflectance spectra for wet process vermilion samples in linseed oil medium exposed to light for ~70 Mlux.h at different relative humidities.

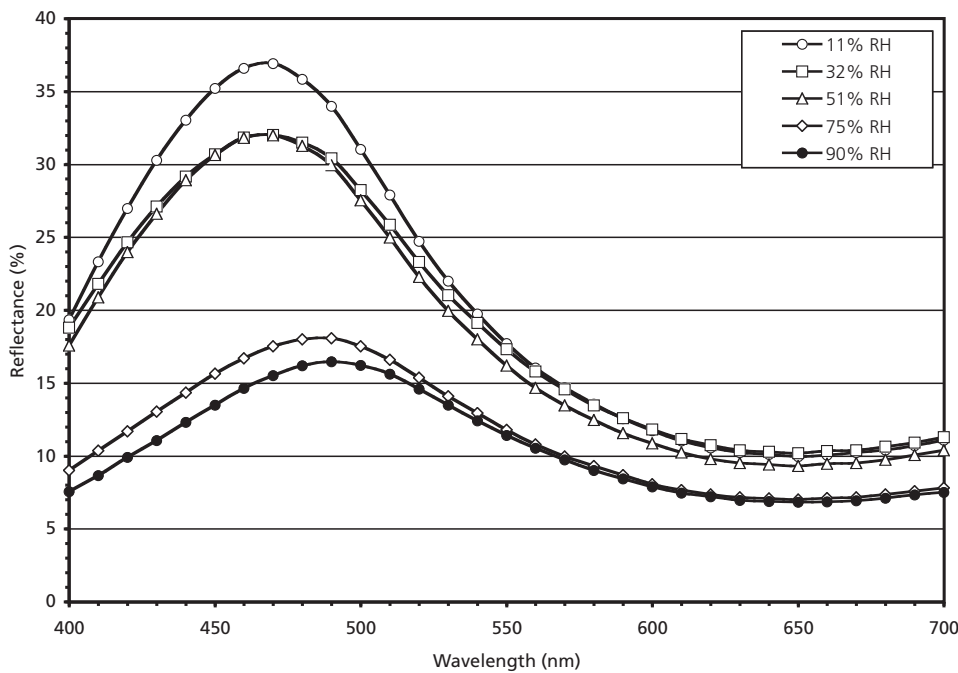


FIG. 6 Reflectance spectra for azurite mixed with salt in glue medium exposed to light for ~50 Mlux.h at different relative humidities.

the same medium, and that the samples bound in egg tempera darkened more than those bound in oil. All the oil-bound samples became rubbery to the touch, whether kept in the light or in the dark. Vermilion is known to accelerate the oxidative degradation of a dried oil film and the behaviour observed in these, very young, films seems to be an example of this.⁵³

The third group of pigments comprises most of the lead-containing pigments studied, including yellow lead monoxide (lead(II) oxide) and red lead.

A detailed description of their behaviour is given elsewhere,⁵⁴ and summarised here. Light-induced deterioration of red lead and yellow lead monoxide led to an initial slight darkening, thought to be caused by the formation of lead(IV) oxide. At lower relative humidities ($\leq 32\%$), this dark product persisted, resulting in an overall reduction in the lightness of the samples. At higher RH ($\geq 51\%$), the samples subsequently lightened as lead(IV) oxide, and the remaining red lead, were converted to lead white (see PLATE 1). These changes occurred more

rapidly in the paint films exposed to light. The rate of change was slightly slower for those samples in binding media that protected the pigment particles most effectively (generally the hydrophobic linseed oil).

Lead-tin yellow type II and lead-tin yellow type I in an oil medium were unaffected by light or RH. One sample of lead-tin yellow type I in tempera showed a slight greying at high RH ($\geq 75\%$), perhaps due to the formation of a little lead dioxide on the surface. It may be that, given a longer exposure, this would have converted to lead carbonate as in the red lead samples.

In the absence of light, chrome yellow darkened slightly, with the greatest darkening at high RH. Samples exposed to light darkened more than those in the dark, but the RH had little effect on the degree of darkening.

The final group of pigments are those that show slight differences in their response to light at extreme (generally high) RH.

Despite many references in the literature to changes in azurite, only two samples showed any alteration in these experiments. A sample in watercolour medium darkened at high RH ($\geq 75\%$). The Fourier transform infrared (FTIR) spectrum lacks peaks in the $650\text{--}400\text{ cm}^{-1}$ region that characterise either copper(II) oxide (tenorite), which has been observed as a deterioration product of azurite,⁵⁵ or copper(I) oxide (cuprite). As the formation of tenorite is reported to occur in basic conditions, its formation in these experiments would be most likely where azurite was mixed with, or painted over, lime, but no changes were observed in these samples. Under the microscope it was clear that the darkening is not superficial, but the FTIR spectrum shows no new peaks that can be attributed to an alteration product, suggesting that this material is infrared inactive. One possibility is copper sulphide, which could be formed by reaction with a sulphide emitted by nearby orpiment samples. However, energy dispersive X-ray analysis revealed very low sulphur levels. Moreover, adjacent lead-containing pigments, which are more susceptible to sulphides, showed no blackening.

The other azurite sample exhibiting change was a mixture of azurite and sodium chloride in glue medium. At high RH ($\geq 75\%$), the samples appear quite green, as shown by PLATE 1 and the reflectance spectra in FIG. 6. The samples at $\leq 51\%$ show maxima in the $460\text{--}470\text{ nm}$ region, while for the samples exposed at $\geq 75\%$, this maximum is shifted toward the green (*c.* 490 nm). A characteristic broad band in the $3354\text{--}3340\text{ cm}^{-1}$ region of the FTIR

spectra indicates that the product formed at high RH is a basic copper chloride, general formula $\text{Cu}_2(\text{OH})_3\text{Cl}$. Unfortunately, the bands in the region below 1000 cm^{-1} that help to identify which basic copper chlorides are present are masked by azurite peaks. In this experiment at least, the only samples in which copper chlorides formed were those in which the azurite was mixed with salt in an aqueous medium; the same mixture in oil showed no colour change. The saturated salts used to create 75 and 90% RH were chlorides (NaCl and BaCl_2 respectively), but there is no evidence of colour change in azurite alone in glue, resulting from deposition of chloride ions from the salt on the surface of the samples, PLATE 1.

Samples of verdigris in linseed oil and watercolour showed changes at high RH. In oil there was a slight browning, particularly visible at the edges of the samples, where the paint layer was thinnest. This colour change is superficial; there were no changes in the FTIR spectra, which continued to be dominated by peaks for verdigris. No peaks for copper carboxylates, tenorite or cuprite were visible. Watercolour samples exposed to light at high RH showed considerable changes; the initial bright blue-green colour faded, giving a cracked, pale green or blue-green powdery surface, PLATE 1. The extreme 'chalkiness' of the surface, which gives high light scatter, may also contribute to the lightening. FTIR spectroscopy indicates that a reaction has occurred, but the products are not easily identified. No carbonate peaks are present, so the formation of a copper carbonate can be excluded. A sharp peak at 3571 cm^{-1} and a shoulder at 3612 cm^{-1} suggest that a copper hydroxide or another basic copper salt may have been formed. Copper(II) hydroxide is pale blue, but the appearance of new peaks in the $1450\text{--}1300\text{ cm}^{-1}$ region suggests rather the formation of a basic copper carboxylate differing from the original (neutral) verdigris.

Although orpiment is said to be affected by water,⁵⁶ there was no evidence that high RH had a similar effect; all the samples of orpiment in watercolour medium lightened on light exposure, irrespective of RH. The samples in oil were unaffected at very low RH (11%), but showed some slight browning at higher relative humidities.

At the beginning of the experiment, the samples of unpigmented linseed oil were sufficiently dry to allow colour measurements to be made using a contact technique. During the course of the experiment, the samples exposed to light at high relative humidities browned and became tacky (51%) or

liquid ($\geq 75\%$). In the dark, the samples at 90% became slightly tacky. The changes in the light at high RH are probably due to both hydrolysis of the ester linkages in the oil triglycerides and a high proportion of photolytically induced cleavages of the fatty acid side-chains. These reactions generate more shorter-chain scission products (than at lower RH or in the dark), which tend to reduce the coherence of the film.⁵⁷

Conclusions

Supporting the findings of previous studies, these investigations have shown that many commonly used pigments exhibit increased light-induced change with increasing RH. For a few pigments the degree of alteration is unaffected by the RH, although these pigments tend also to be those least susceptible to light-induced colour change. Hydrophobic or more medium-rich films, which better protect the pigment particles, seem less prone to damage at high RH.

Many of the changes observed at high RH mirror those reported in the literature, for example the conversion of red lead to lead white. Other changes are clearly dependent on a more complex set of circumstances and rely, for instance, on the presence of liquid water, the passage of dissolved salts, or an unusually high pH. These conditions are all more likely in wall paintings, thus the changes observed in these experiments occur more frequently in this context, but very rarely in easel paintings, even those stored in what seem very damp conditions. Many paintings now in museums and galleries were originally part of decorative schemes that were quite close to, but not in contact with, walls. These show few signs of having suffered, despite their proximity to moisture and salts; indeed, from the sixteenth century, canvas was used as a support for decorative schemes in Venetian *palazzi* to avoid such damage.

There are several reasons why experimental results may not correspond exactly to changes seen in paintings. Experiments are normally of short duration, compared to the age of most paintings. The pigments used, although fairly wide in range, did not necessarily correspond to the varieties used by artists, an example being the neutral verdigris used in the experiment: artists may have used a basic form. Changes seen in the samples might resemble those observed in paintings, but they may arise from a completely different chemical reaction. For example, the darkening of azurite observed in

the experiments does not arise from the formation of tenorite reported in the literature, demonstrating the danger of relying only on the results of such experiments to explain phenomena observed in the field.

As it is uncommon to find an easel painting whose history, including its conservation history, is known from the time it was painted, it is not usually possible to say with certainty that an observed change results from exposure to damp conditions. However, the results from experiments can alert us to changes that might have occurred, or may still be occurring.

The liquefaction of the oil medium at high RH, which was observed in some samples, is a phenomenon that deserves further study, but it should be stressed that the oil paint films examined in these experiments were young when exposed to high RH. It is worth bearing in mind, however, that some easel paintings could have experienced such conditions early in their history, and conceivably passages in these paintings were adversely affected as a result. Although there is no direct evidence, this phenomenon might be the root of some paint defects that are observed in one or two colours on a painting that is otherwise very sound.

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