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Front cover: *The Virgin and Child before a Firescreen*,
detail of Plate 1, p. 20.

Light-induced Colour Changes in Red and Yellow Lake Pigments

DAVID SAUNDERS AND JO KIRBY

A cursory glance around the walls of any collection of western European paintings, dating from any time between the fourteenth and nineteenth centuries, will reveal numerous examples of the use of red and yellow lake pigments – translucent pigments prepared by the precipitation or adsorption of an organic dyestuff onto an insoluble substrate. Lake pigments, notably the reds, gave depth and transparency to the richly glazed shadows of draperies; red lakes were mixed with, or glazed over, white and blue to give delicate pinks and mauves; combined with yellows, browns or blues, yellow lakes gave subtle yellows and greens. Lake pigments were an essential constituent of the artist's palette.

The most casual visitor to the National Gallery could not fail to notice the striking portrait of *Anne, Countess of Albemarle* (NG 1259), painted by Sir Joshua Reynolds around 1760 (Plate 1 and Fig. 1).[1] The Countess is seated in front of a deep purplish-red curtain. Her level gaze is indicative of a formidable personality; the deep pallor of her face, enlivened only by two spots of pink on her cheeks, does not, however, suggest the robust constitution of one who made a complete recovery from a stroke in 1780, at the age of 77.[2] Examination of a cross-section prepared from a sample taken from a small loss in the paint of her cheek provided the explanation for Lady Albemarle's pallor: the paint, composed of lead white mixed with a red lake pigment, had originally been pink, but the red has faded almost completely, apart from a pink particle at the bottom of the paint layer in the cross-section. It is not immediately apparent that the paint of the curtain, which is glazed with a red lake pigment, has also faded slightly, but the colour is deeper where the paint has been protected from light by the rebate of the frame.

Reynolds was repeatedly warned by his contemporaries about the impermanence of some of his pigments, yet 'lake' appears regularly in contemporary notes on the pigments he used.[3] In March 1755, the poet William Mason, observing Reynolds at work on a portrait, recorded the presence of lake on the artist's palette, mixed principally with lead white for the flesh and alone for the sitter's crimson drapery. He noted that, while the flesh paint of the face soon faded, the lake used in the glaze of the sitter's crimson

Plate 1 Sir Joshua Reynolds, *Anne, Countess of Albemarle* (NG 1259), *c.* 1760. Canvas, 126.9 × 101 cm. Detail of Lady Albemarle's face.

coat held its colour better. Criticising the painter's use of lake, he wrote: 'But using, as he did, that vegetable or animal pigment, the solving matter of which may be either Brazil wood or cochineal, on a white earthy basis, it is no wonder that they faded; for it is highly reasonable to think that those pigments, whose hue is either originally inherent in them, or fixed by fire . . . must be more durable than chalky or aluminous earths, to which a colouring dye is given by simple decoction . . .'[4] Although it has not been possible to examine the red pigment used in the painting of the Countess of Albemarle's flesh, analysis by high-performance liquid chromatography has confirmed the presence of the dyestuff obtained from cochineal, and the absence of brasilwood dyestuff, in the red lake used to paint the curtain. Mason's description of

Fig. 1 Reynolds, *Anne, Countess of Albemarle.*

the subsequent behaviour of the lake in the two areas is fairly typical, as will be described below.

Loss of colour in red lake pigments has often been observed. Reynolds was not the only eighteenth-century English painter whose work suffered from this defect: in Thomas Gainsborough's portrait *Dr Ralph Schomberg* (NG 684), painted in the early 1770s, the crimson glaze paint of the sitter's red coat has also faded. In this case too, the red lake contained cochineal dyestuff.[5]

Fading of a lake pigment may result in more emphatic modelling of a figure. The effect of fading of a layer of red lake paint, glazed over a white underpaint in thicker or thinner layers, may be seen in the red robes of a number of the figures in the San Pier Maggiore Altarpiece, painted in Florence in 1370–1 by Jacopo di Cione and his workshop (NG 569–578). An example is the salmon pink robe of Christ in the central main panel, *The Coronation of the Virgin, with Adoring Saints* (NG 569): the main body of the robe is very pale, with few mid tones, while the shadows are startlingly red (Plate 2). Examination of a paint sample taken from the shadow outlining the robe of Saint Reparata (at the extreme left, in the back row of

saints in the left-hand panel) shows that here, where the colour of the lake is still strong, the glaze layer over the lead white underpaint is relatively thick.[6]

Paler tints of red may also be obtained by the admixture of varying amounts of white; an example of the result can be seen in the robe of Saint John the Evangelist (on the right in the second row of saints in the same panel as Saint Reparata). In this case lac dyestuff was used for the preparation of the pigment. The latter method can be used in the preparation of pale, middle and deep tones of purple, incorporating a blue pigment, such as the mineral pigments ultramarine or azurite, in the mixture. An example of the result may be seen in the lilac robe of Saint Clare, standing in front of Saint Reparata; in this case the blue component of the mixture is ultramarine. Azurite, which is a greener blue, would give a more muted colour.[7]

In a number of paintings, the red lake component of such mixtures has been lost, resulting in a profound change in appearance, which differs from the artist's original conception. An example is the robe of the Virgin Mary in *The Virgin and Child before a Firescreen* (NG 2609; see Plates 1 and 6, p. 20 and p. 32): now almost white in colour, apart from its rather cold purplish shadows, it would once have been a warmer colour, perhaps a mauve tone.[8] A similar change of colour has occurred in the robe of the Virgin in *The Coronation of the Virgin* (NG 1897), the central panel of an altarpiece painted, perhaps around 1414, by the Camaldolese monk Lorenzo Monaco. The original colour of the robe was pinkish mauve (it survives beneath the mordant gilding), but it now appears white due to the loss of colour in the lac lake used.[9] The same change has been reported in several other fourteenth- and early fifteenth-century Florentine panels and the point has been made that, particularly in examples such as these, the fading of the red lakes has had significant consequences as far as the interpretation of the paintings is concerned, both aesthetically and iconographically.[10]

Yellow lake pigments have often been used in so inconspicuous a way that any change in their colour may pass unnoticed. The absence of the yellow component from those mixtures where a green is the intended result is the most obvious. This was noted by J.-F.-L. Mérimée, writing in 1830, who commented that in general yellow lakes had little stability: 'One sees, in several Flemish paintings, leaves of trees have become blue, because the yellow lake, mixed with ultramarine, has disappeared.'[11] A probable example of what he had in mind can be seen in the dark blue-green foliage of Pieter Lastman's *Juno discovering Jupiter with Io* (NG 6272), dated *c.* 1618. Examination of a fragment of paint under the microscope revealed that here the blue pigment is azurite,

which is a greenish blue in any case; a few yellow ochre and lead-tin yellow particles are also present, together with what are probably particles of a yellow lake pigment.[12]

Something rather similar may well have happened in *A Child with an Apple* (NG 1020), painted by Jean-Baptiste Greuze (1725–1805) perhaps towards the end of his career, where the apple is now a rather unappetising blue colour (Plate 3).[13] Examination of the painting under a stereomicroscope at a magnification of 40x suggested the presence of lead white and, probably, Prussian blue in the areas that might have been expected to be green, but no yellow pigment could be discerned. As no further analysis was possible, the presence of a now-faded yellow lake pigment cannot be confirmed.

A more subtle change has occurred in the foreground of 'The Large Dort' (NG 961), by Aelbert Cuyp, painted around 1650 (Fig. 2).[14] Several areas of greenish paint in the lower part of the painting are greyish and streaky in appearance. A cross-section prepared from a tiny sample of grey-green foliage paint, taken from a damage on the lower left of the painting, showed that the top layer of paint consisted of a translucent yellow lake pigment, mixed with small quantities of other pigments, including yellow ochre. While the original yellowish colour of the paint is still apparent at the bottom of the layer, it has been lost at the top, which appears white (Plate 4, p. 84). Energy-dispersive X-ray microanalysis of the cross-section suggests that the substrate of the lake pigment may be chalk, perhaps derived from a white earth or marl (rather than from some other source of calcium carbonate such as ground cuttlefish bone).[15]

As examination reveals an increasing number of paintings in which colour changes such as those described above have taken place, it is important to have some understanding of how the lake pigments behaved and in what way they are likely to have changed. Errors or misunderstandings in the interpretation of the paintings may thus be avoided.[16] If the pattern of changes in the pigments can be recognised, it should be possible to minimise them in the museum environment by paying particular attention to light levels and by excluding ultra-violet radiation.

The impermanence of natural organic dyestuffs, both as lake pigments and as textile dyes, was already well known by the early nineteenth century. Colour change of dyestuffs had rather greater implications for the textile industry and it is not surprising that it was in this field that early research into possible causes of fading was first carried out.[17] The most wide-ranging recent study of the lightfastness of natural dyestuffs dyed on wool or cotton using different mordants is that of Padfield and Landi.[18] A number of other general studies of textile dyestuffs, concentrating on the

Plate 2 Ascribed to Jacopo di Cione and Workshop, *The Coronation of the Virgin, with Adoring Saints* (NG 569), 1370–1. Wood, central panel, pointed top, painted area 206.5 × 113.5 cm. Detail of Christ's robe.

Plate 3 Jean-Baptiste Greuze, *A Child with an Apple* (NG 1020), *c.* 1800. Canvas, 40.6 × 32.1 cm.

Fig. 2 Aelbert Cuyp, *A Distant View of Dordrecht, with a Milkmaid and Four Cows, and Other Figures ('The Large Dort')* (NG 961), *c.* 1650. Canvas, 157.5 × 197 cm.

quantitative description and measurement of colour change[19] and rates of fading of the dyestuffs,[20] also have some relevance to the study of lake pigments. However, it is not necessarily the case that a dyestuff which has relatively good stability on a textile, using a particular mordant, has equal stability as a pigment on the equivalent substrate. In practice, stability is a property of the dyestuff/substrate/medium system – or dyestuff/mordant/ fibre system – rather than that of the dyestuff alone.

The earliest systematic experiments on the effect of exposure of pigments to light, polluted air and moisture were carried out by George Field from 1809 onwards. He tested samples in oil and in watercolour, comparing the results with identical samples kept in the dark. His light-exposed samples were kept in the sun 'till a like specimen of the cake lake of the London Colourmen is destroyed'.[21] Although Field's results are not graded into degrees of permanence and are not comparable to modern standards, they are of interest because he was able to test samples of kermes and lac

lakes, for example, which were unavailable to later workers.[22]

While a number of studies on artists' pigments were conducted later in the century,[23] the most thorough investigation was that of Dr W. J. Russell and Captain (later Sir) W. de W. Abney, carried out from 1886 to 1888.[24] The report was based on a study of the effects of light, both natural and artificial, on watercolour pigments, including carmine and a number of madder lakes, under atmospheric conditions and in a vacuum. Later investigations of the lightfastness of modern pigments by Vesce[25] and Levison[26] have examined the effects of different paint media and the addition of white. Many of the more recent studies on colour change in pigments prepared using traditional organic dyestuffs have been concerned with Japanese prints; these have included research into the effects of various atmospheric pollutants.[27] Particularly relevant to the present study is the work of Ruth Johnston-Feller on the behaviour of alizarin crimson, as a glaze or mixed with white.[28]

It has to be borne in mind, however, that modern lake pigments, even alizarin crimson, bear only a fleeting resemblance to their antecedents. Even assuming that the madders studied by Russell and Abney were still derived from the natural dyestuff, and not from synthetic alizarin, late nineteenth-century methods of dyestuff extraction were considerably more effective and sophisticated than those of earlier times. As far as the more expensive red dyestuffs, derived from the scale insects kermes and both Old and New World cochineal, were concerned, documentary sources suggest that an indirect method of extraction of the dyestuff from cloth shearings was used from about the late fourteenth to the late sixteenth century and possibly longer; this may affect the stability of the dyestuff. Studies of modern fugitive organic pigments have indicated that different precipitating salts influence their stability to light;[29] while it is very likely that traditional pigments behave similarly, the precise differences in the behaviour of the same natural dyestuff on different substrates have not been quantified, although parallel studies on textile dyestuffs have been made.[30]

The work described in this article is concerned with light-induced fading; it is certainly true that chemically induced fading, caused by atmospheric pollution for example, could result in changes to the appearance of paintings similar to those described above. The rebate of the frame might partially protect the edge of the painting from chemically-induced colour change as it protects it from colour change caused by light. In certain circumstances the effect of pollutants must be borne in mind, but in a museum environment, visible light and ultra-violet radiation are likely to play a considerably greater part.

Preparation of samples

Dyestuffs

The red and yellow dyestuffs selected for this study were derived from both plant and insect sources and are representative of the materials used in easel paintings up to and including the early nineteenth century. Lake pigments were prepared on a small scale following western European recipes dating from the early fifteenth to the early nineteenth century (see Appendix).[31] The red dyestuffs selected were cochineal, kermes, lac, madder and brasilwood. The yellow colorants were extracted from unripe buckthorn berries, quercitron and weld. In addition, a commercial sample of alizarin crimson was included in the experiments to provide a point of comparison with other studies of the fading of organic red materials.

Method of dyestuff extraction

One factor that may affect the stability of lake pigments is the method by which the dyestuff is extracted from the raw material. The simplest, and most direct, method is to extract the dyestuff from the raw material with water or an alkali. The soluble dyestuff components are then converted into the insoluble lake pigment. Some variant of the direct method is normally followed in the preparation of yellow lake pigments. Lake pigments from all eight dyestuffs studied were prepared in this manner.

An alternative method is to extract the colorant from clippings of dyed textile using alkali. The textile would have been dyed in the normal way, extracting the dyestuff with water in a dye bath and mordanting it onto the desired fabric – silk or wool, for example – using alum or alum and cream of tartar.[32] Clippings or other textile waste were then used as the source of dyestuff, which was extracted using a lye of ash or similar alkaline solution. The pigment was then precipitated by the addition of alum. A study of contemporary recipes suggests that this was the principal method for the preparation of lake pigments from kermes, cochineal and related scale insects (apart from lac) from the late fourteenth to at least the late sixteenth century. There appear to be very few recipes for the preparation of these lakes by direct extraction of the dyestuff from the raw material dating from this period. For kermes lake, the colour obtained by the indirect method is certainly a less brown and more scarlet red, but undoubtedly economic and other factors were involved in the choice of this method. Similarly, there are very few recipes at all for madder lakes during the same period; the indirect method of preparation may have been of greater importance.

To emulate this process, wool was dyed with kermes, cochineal, lac or madder using an alum and cream of tartar mordant. Clippings from each of the dyed wools were treated with an alkaline solution to extract the dyestuff; the coloured solution was then treated with alum to precipitate the pigment (see Appendix).

Substrates

Before the early nineteenth century the substrate for lake pigments was generally white and translucent when dispersed in the binding medium. The common substrate, formed by precipitation as described above, was hydrated alumina, but this was by no means the only possibility. Frequently a calcium salt, usually some form of calcium carbonate, was added to the solution of dyestuff and alum in place of, or in addition to, the alkali. The resultant substrate would then contain a precipitated calcium salt as well as the aluminium salt. If excess calcium salt was added it would not have reacted but would have passed into the final pigment as an extender. On occasion lakes were prepared by adding a calcium salt, a white
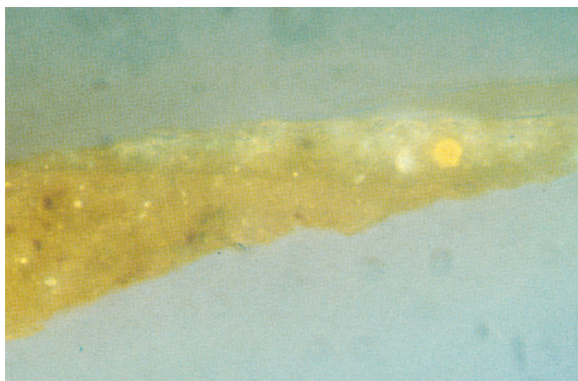
Plate 4 Aelbert Cuyp, *'The Large Dort'* (see Fig. 2). Cross-section of grey-green foliage paint, showing fading at top of upper layer of yellow glaze, below a trace of the varnish layer. The glaze retains its colour at the bottom of the paint layer. The lower layer contains a yellow lake pigment mixed with other pigments, including yellow ochre and bone black (ground layers missing). Photographed under the microscope by reflected light at a magnification of 750×; actual magnification on the printed page 550×.

chalk-containing clay or other inert white material to the dyestuff solution. In these cases very little aluminium compound would be present in the final pigment. In such pigments the chemical bonding between the dyestuff molecule and the inorganic substrate might be less strong than in pigments where the substrate is precipitated during the reaction. Calcium-containing substrates, which also have an effect on the final pigment colour, are often found in recipes for yellow lakes and those derived from brasilwood.

To investigate the effect of substrate on the behaviour of lakes of a particular dyestuff, each of the yellow lake pigments was prepared on two different substrates. The first was produced by adding alum and alkali to the dyestuff solution, while the second was prepared from the same batch of raw material but using alum and chalk. Two lakes of cochineal dyestuff were prepared in a similiar manner. In addition, an early nineteenth-century recipe was followed in the preparation of a third cochineal lake in which the substrate was freshly prepared tin(IV) oxide (see Appendix). (There is little evidence for the availability of any tin-containing cochineal lake before the very late eighteenth or early nineteenth century.)

Media
The paint medium serves to bind the pigment particles together and to the support; it forms a coherent coating when dry. It also protects the pigment particles from physical or chemical damage to a greater or lesser extent. Three paint media were used to prepare the samples in this study, namely watercolour, egg tempera and linseed oil. Watercolour samples were prepared by grinding the pigment in a freshly made solution of gum arabic to give a fairly stiff paint. Two to four layers of paint were applied to Whatman Silversafe 200gm^{-2} conservation grade paper to give complete hiding.[33] Alternatively, the gum arabic paint was diluted with distilled water and applied as a thin wash on the same paper.

Egg tempera samples were prepared by grinding the pigments in a 1:1 (v:v) mixture of egg yolk and water.

The resulting paint was applied to one of two supports. The first was a wood panel coated with eight thin layers of gilder's whiting (calcium carbonate) in rabbit skin glue; when dry this was rubbed down with abrasive paper. It was finished by polishing with a cloth. The second support was Silversafe paper as used for the samples in watercolour. In each case the paint layer was sufficiently dense to give complete hiding of the support.

Oil paint samples were prepared by grinding the lake pigments in Winsor and Newton linseed oil containing a manganese-based drier: lake pigments are poor driers. The samples were applied either to a panel, prepared as described above, or to paper that had previously been coated with a lead white/linseed oil priming to prevent the oil from the paint layer being absorbed by the paper. Again the samples were of a thickness sufficient to give complete hiding. Before any exposure to light in the fading chamber, the samples were allowed to dry for two to three months in conditions such that light was excluded as far as possible, while air was still able to circulate freely to allow the initial polymerisation of the oil to take place.[34] After this time the paint was 'touch-dry' and firm enough to permit the measuring head of the chroma meter to be placed on its surface without damaging the paint film.

Mixtures of lake pigments with white
In order to examine the effect of combinations of lake pigments with white, a number of samples were prepared by mixing the lake pigment with different proportions of lead white. Lead white was chosen for this study as it was the most commonly used white pigment in easel painting from the earliest times and is still in use today, in spite of the availability of less toxic titanium white.

Mixtures of lake pigment with lead white were made by grinding the pigments together in distilled water. Lake pigment to lead white ratios from 1:1 to 1:50 (w:w) were used. The mixtures were then thoroughly dried. Samples of each were then applied in

drying oil or in egg tempera to a prepared panel. A selection of the mixtures was also applied to Silversafe paper as a tempera or watercolour film. The same mixtures were applied in oil to lead white primed paper. In each case the layer was dense enough to give complete hiding of the support.

Light exposure

The samples were exposed to artificial daylight at an illuminance of 10,000 lux. The sources used in the ageing chamber were Thorn Artificial Daylight fluorescent lamps. In order to ensure that the spectral characteristics of the source were reasonably consistent, the lamps were run for 100 hours prior to use in the fading chamber and were discarded after 3000 hours of operation. The fading chamber was ventilated to maintain the temperature inside at a constant value (*c.* 32°C). The relative humidity within the chamber was 40±5%. As a rough guide, 60 hours' exposure in the chamber is equivalent to one year on exhibition, assuming that the illuminance is maintained at the current recommended level of 200 lux, that the object is illuminated for eight hours each day, and that there is no filtration of ultra-violet light.

A number of samples of lake pigments in watercolour wash were faded in daylight and in the fading chamber described above. The relative rates of fading of the different pigments were the same in each case.

Those samples that were to be exposed to light from which the ultra-violet radiation had been filtered were placed beneath a 3 mm thick polycarbonate sheet.[35] A duplicate set of samples was placed in the fading chamber within an opaque enclosure to act as a dark control. To allow results from different experiments to be correlated, ISO blue wool standards numbers 1 to 3 were included in the experiments.[36]

Colour measurement

The colour of each sample was recorded prior to exposure and periodically during the experiment. The basic instrument used for colour measurement was a Minolta CR200 series chroma meter.[37] For matt samples, for example those in watercolour medium, the meter was used in conjunction with a CR200 measuring head, which provides diffuse illumination and measures the reflected light perpendicular to the surface of the sample (this standard measuring geometry is referred to as d/0: diffuse illumination with measurement at 0°). The CR200 head measures a sample area 8 mm in diameter. For glossy samples, particularly those in oil medium, the d/0 measuring geometry is not suitable. In these cases the meter was used with a CR221 head, which has a 45/0 geometry. Since the sample is illuminated at 45° and the reflected light measured perpendicular to the surface, the gloss or specular component is excluded

from the colour measurement. The measuring area for the CR221 head is 3 mm in diameter.

The microprocessor in the meter was used to convert these measurements into Commission Internationale de l'Eclairage (CIE) L*, a* and b* coordinates under the CIE standard illuminant D65.[38] The three coordinates correspond to three attributes of a colour. L* represents the lightness of a colour on a scale from 0 (black) to 100 for a pure white. The a* coordinate represents a red-green scale. A positive value for a* indicates redness, while a negative value symbolises greenness. In the same way, b* is a yellow-blue scale with positive values of b* signifying yellowness. These data were transferred from the meter for permanent storage on a computer.

The colour difference (ΔE) between the sample prior to light exposure and at each measurement during the experiment was calculated using the colour difference equation developed by the Society of Dyers and Colourists Colour Measurement Committee (CMC) and accepted as British Standard 6923:1988.[39] All the colour differences which follow are derived according to this method.

The error in colour measurement depended on the homogeneity of the sample and the size of the area measured. For the samples in watercolour wash, which had a fairly uniform, matt appearance and could be measured using the CR200 head, the error in measurement was low, ΔE ±0.25. For the thick watercolour samples and those in egg tempera or oil medium, the error was rather higher (ΔE ±1.3) due to a combination of a less uniform surface and the smaller measuring area of the CR221 head. These errors were most apparent in the intensely coloured pure lake pigment samples in oil medium.

Results and discussion

The colour changes measured for the dark control samples were all negligible in the context of the error introduced by the measurement process. These results suggest that there were no temperature- or humidity-induced colour changes.

The most obvious colour changes observed for the lake pigments were an increase in lightness and a decrease in redness or yellowness for the red and yellow pigments respectively. This fading is most apparent in the thin watercolour washes because of the low concentration of pigment.

It is known that oil films yellow when kept in the dark: an initial, reversible, change in the colour of the oil film will have occurred during the drying process, but before measurement commenced. In those samples exposed to light, this yellowing is 'bleached out' in the first 48 hours of exposure. No colour change was detected for the control samples. The expected long-term and irreversible increase in yellowness as the
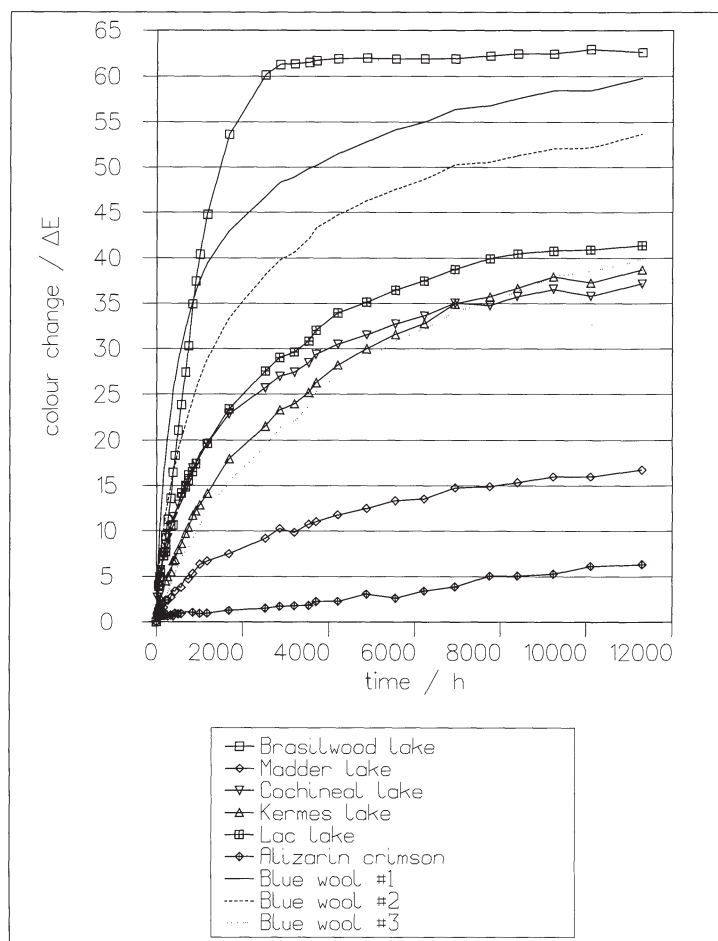
Fig. 3 Colour change against time for red lake pigments on aluminium-containing substrates painted out as watercolour washes. The colour change curves for alizarin crimson and for blue wool standards numbers 1 to 3 have been included for comparison.
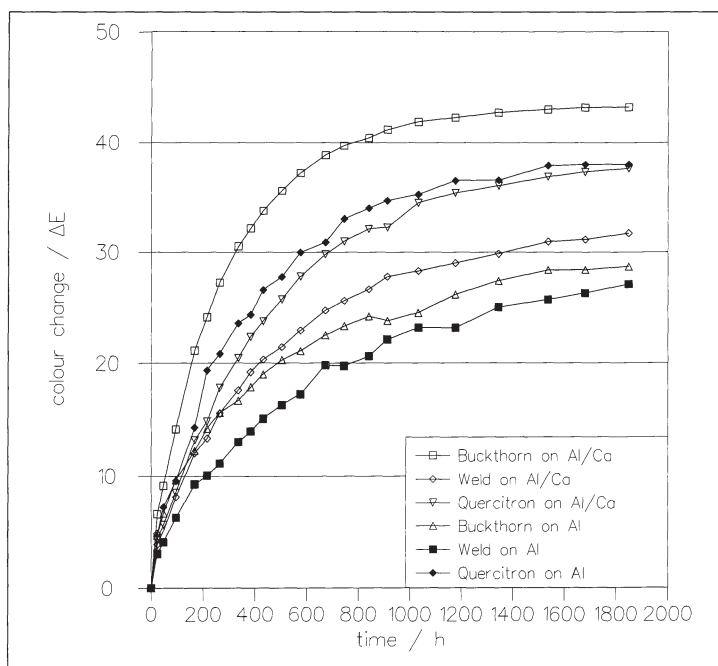

Fig. 4 Colour change against time for yellow lake pigments on aluminium- and calcium/aluminium-containing substrates painted out as watercolour washes.

film polymerises was not measurable over the time of these experiments.[40]

The effect of dyestuff

For any given substrate – and hydrated alumina is perhaps that most commonly used to prepare red lakes – there is a clear order of stability for the pigments prepared from anthraquinone dyestuffs, including alizarin. For these pigments, the stability to light decreases as the degree of substitution increases.[41] Brasilwood, the colour of which derives from the arylchroman brazilein,[42] is invariably less stable even than the most fugitive of the anthraquinone dyestuffs on the same substrate. Fig. 3 shows the colour change on light exposure for a series of red dyestuffs prepared as lake pigments on alumina and painted out as thin watercolour washes on paper.

The curves in Fig. 3 illustrate the fugitive behaviour of brasilwood lake. The commercially prepared sample of alizarin crimson is most stable, followed by the madder lake prepared in the laboratory (in this case, the dyestuffs had been obtained by direct extraction from the appropriate raw material). The figure also shows the rate of fading of blue wool standards numbers 1 to 3 for comparison. The three dyestuffs derived from scale insects are markedly less stable than the less highly substituted anthraquinones contained in the madder dyestuffs.

The pattern of stability is less clear for the yellow lakes and depends more critically on the nature of the substrate. Of the three flavonoid dyestuffs studied, that extracted from weld appears to be the least fugitive.[43] Fig. 4 shows the light-induced colour change for these three pigments on both aluminium- and mixed aluminium/calcium-containing substrates. The effect of the substrate on the relative stability of the pigments is discussed below. Figs. 3 and 4 show only the total colour change with time. Although the principal effect of fading is an increase in lightness (L*), it is necessary to follow the change in red-greenness (a*) and yellow-blueness (b*) to assess the overall change in colour. For example, Fig. 5 shows the changes in a* and b* which accompany the increase in lightness for five red pigments as watercolour washes.

The sample of madder shows a decrease in both yellowness and redness from the beginning of the experiment, but with the loss of yellow proceeding more rapidly than that of red. This would suggest that any yellow components of the dyestuff, and any yellow intermediates formed during the fading process, are destroyed more rapidly than the red components.[44]

For the three insect dyestuffs, the loss of redness is accompanied by an initial increase in yellowness followed by a gradual decrease in yellowness as fading continues (the particular cochineal sample illustrated

had barely begun to decrease in yellowness at the end of the measurement period).

The pattern of colour change for the lac, kermes and cochineal samples suggests that during the initial stages of the fading process one or more yellow intermediates are produced by the destruction of the red component(s). As the fading proceeds, the concentration of yellow material reaches a steady state before decreasing as the concentration of the red precursor material(s) diminishes. In view of the behaviour of madder, described above, it seems unlikely that the colour changes in the insect dyestuffs can be attributed to the more rapid fading of their red components.

During the first part of the experiment the brasilwood sample increases in yellowness as the redness decreases, giving a brownish appearance during fading. Only after most of the redness has disappeared does the yellowness begin to decrease. This last colour change is shown by all the brasilwood samples, including the densely pigmented sample in oil medium. Since brasilwood dyestuff is thought to consist mainly of a single colorant, brazilein, it seems probable that the increase in yellowness results from the formation of an intermediate breakdown product.

Fig. 6 shows a plot of a* against b* for the three yellow dyestuffs as lake pigments on calcium/aluminium-containing substrates. All three behave in a similar manner; the yellowness (b*) steadily decreases throughout the experiment as the lightness increases. In contrast, the redness (a*) increases during the first 48 hours of exposure, then decreases slightly before increasing during the remainder of the experimental period.

While these changes in colour do not elucidate the nature of the changes in the dyestuff molecules, the dark control samples show no shift in a*, which indicates that the initial increase in redness (decrease in greenness) is indeed light-induced and not due to any slight rise in temperature.

The effect of the method of extraction
As described above, samples of cochineal, kermes, lac and madder lakes were prepared both by direct extraction of the dyestuff from the raw material and indirectly from wool clippings. Fig. 7 shows the colour change with respect to time for these eight samples. With the exception of the lac lakes, which fade at rather similar rates, the lake pigments prepared directly from the raw material fade less quickly than the comparable samples prepared from wool clippings.

One possibility is that the dyestuff is fractionated by dyeing on the wool substrate and that the proportion of components in the material extracted from the wool is rather different from that produced by direct extraction from the raw material. It may also be that
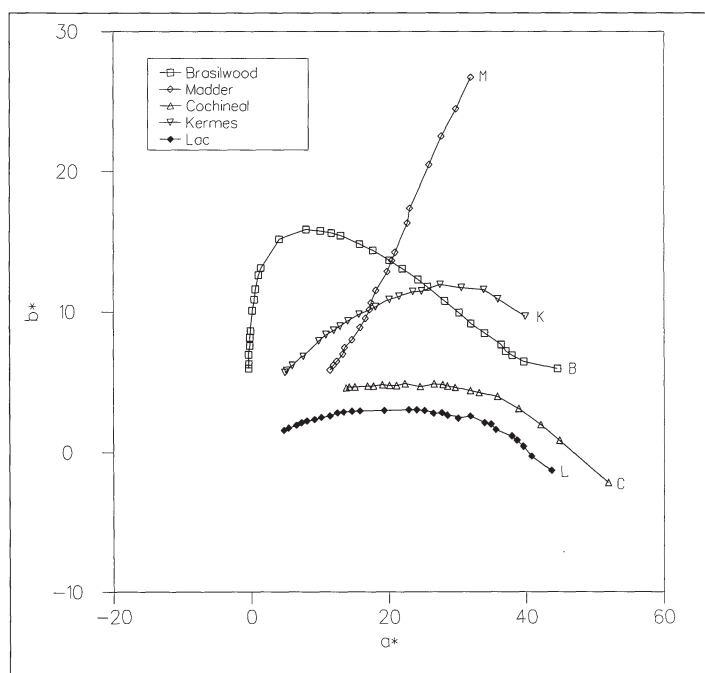

Fig. 5 Changes in redness (a*) and yellowness (b*) on exposure to light for red lake pigments on aluminium-containing substrates painted out as watercolour washes. The labels are adjacent to the points representing the colour of each sample before light exposure.

Fig. 6 Changes in redness (a*) and yellowness (b*) on exposure to light for yellow lake pigments on calcium/aluminium-containing substrates painted out as watercolour washes. The labels are adjacent to the points representing the colour of each sample before light exposure.
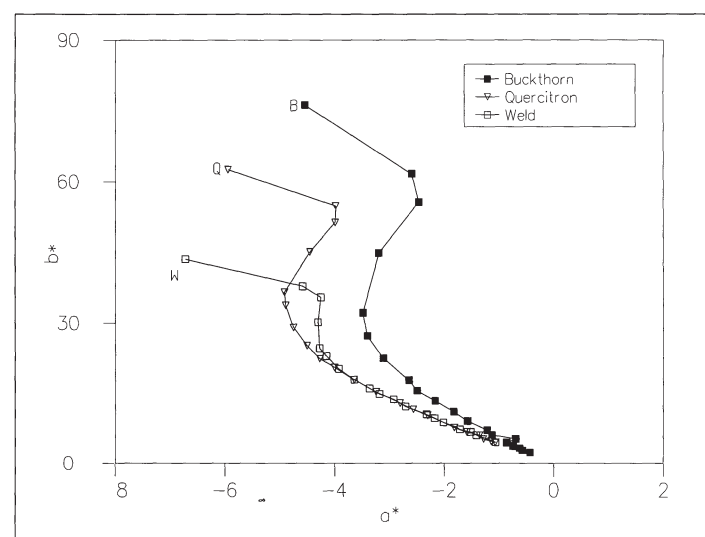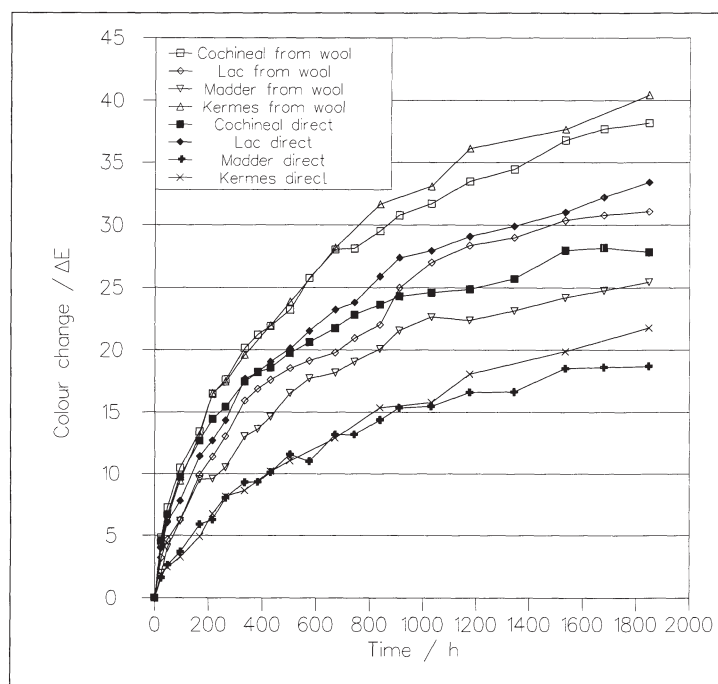
Fig. 7 Colour change against time for red lake pigments on aluminium-containing substrates painted out as watercolour washes. Comparison of pigments prepared from dyestuffs obtained by direct extraction with those obtained from wool clippings.

Fig. 8 Changes in redness (a*) and yellowness (b*) on exposure to light for red lake pigments on aluminium-containing substrates painted out as watercolour washes. Comparison of pigments prepared from dyestuffs obtained by direct extraction with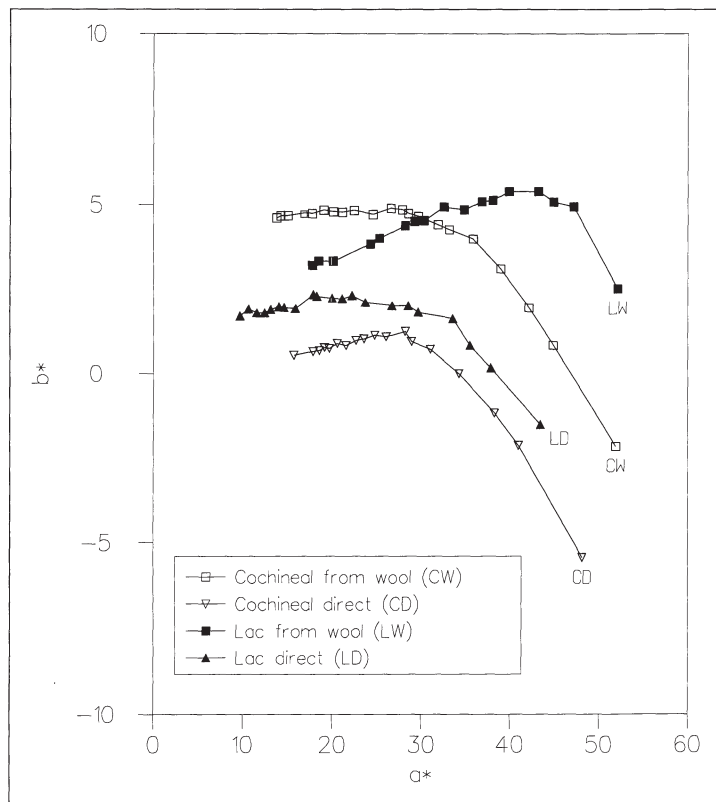 those obtained from wool clippings. The labels are adjacent to the points representing the colour of each sample before light exposure.

the proportion of more fugitive components is higher in the wool-extracted material: this appears to be the case in the madder lakes tested.[45] A second explanation for the difference in stability is that the dyestuff molecule is attached to the lake pigment substrate in a different manner from that resulting from the direct preparation. This might be because the sites on the dyestuff molecule which would normally be attacked by alkali during the extraction from the raw material are bonded to the mordant in the dyed wool intermediates.[46]

Whatever the change in the dyestuff composition or binding, a comparison of the a* and b* data for samples prepared by the two methods of extraction reveals that there is no appreciable difference in the pattern of colour change exhibited by the colorants as they fade (see Fig. 8).

The effect of lake substrate

To assess the effect of the substrate upon the stability of red lake pigments a series of cochineal lakes was studied. Three cochineal lakes were made with substrates consisting essentially of hydrated alumina, hydrated alumina with a calcium salt (largely $CaSO_4$), and freshly prepared tin(IV) oxide. In addition, a sample of cochineal carmine (in this case the aluminium/potassium salt of carminic acid, prepared according to an early nineteenth-century recipe) was studied.

Fig. 9 shows the fading with time of these four pigments. It is clear that the sample of cochineal carmine is more stable than any of the lake samples and that of these, the tin-containing lake is the most fugitive. Of the two aluminium-containing lakes, that which also includes a calcium salt is less permanent.

A similar pattern of behaviour was observed for the yellow lake pigments with aluminium- or aluminium/calcium-containing substrates. It can be seen from Fig. 4 that buckthorn, quercitron and weld lakes on hydrated alumina are more stable than the analogous lake pigments containing some calcium salt. It is apparent that when a calcium salt (in the form of $CaCO_3$) is added to the extracted dyestuff, the resulting lake pigment is more fugitive. It seems that the calcium 'complexes' of the flavonoid or anthraquinone dyestuffs are less stable than those of aluminium.[47]

The role of the calcium salt may not be confined to the formation of 'complexes' with the dyestuff. If $CaCO_3$ is added in excess – and in many recipes ground marble, cuttlefish bone or similar sources of $CaCO_3$ are added 'to taste' – then it will act as an extender. The effect of extender is illustrated in Fig. 10, which shows the fading with time of three lakes, all prepared from the same sample of unripe buckthorn berries. In lake No. 1, on a substrate of hydrated alumina, the amount of substrate precipi-

tated during the formation of the pigment was insufficient to combine with all the dyestuff present, resulting in a deep yellow lake; the excess dyestuff remained in solution. In lake No. 2, also on hydrated alumina, the suggested quantity of ingredients resulted in a somewhat lighter, bulkier product due to the presence of a slight excess of hydrated alumina, acting as an extender. There was no residual dyestuff. Lake No. 3 has a calcium/aluminium-containing substrate. It is apparent from the curves in Fig. 10 that although the first two lakes contain the same substrate, the presence of excess substrate (extender) in lake No. 2 reduces its stability; the calcium-containing lake is still by far the most fugitive.

The effect of the support

The experiments indicated that the support played little or no part in determining the rate of colour change. Equivalent egg tempera samples painted out on paper and on primed panel faded at similar rates. Equally, samples painted out in oil on primed paper or on primed panel behaved in an analogous manner.

Fig. 11 shows the fading of pairs of lac/lead white and madder/lead white samples in oil medium, painted out on primed paper and on panel.

The effect of medium

The samples of lake pigment, unmixed with white, which showed the most rapid change of colour during the course of the experiment were those painted out as thin watercolour washes. That this effect is the result of the thinness of the paint layer and low pigment density rather than of any particular property of the gum arabic medium is demonstrated by the behaviour of the watercolour samples with greater pigment density. These latter samples, which were painted out thickly, and even showed good gloss due to the higher concentration of medium, faded more slowly than the egg tempera samples and at approximately the same rate as the samples in oil. The minute quantity of gum arabic present in a thin wash gives negligible protection to the pigment particles. The fugitive behaviour is compounded by the considerable amount of light reflected from the white paper support.

Fig. 12 shows the rate of colour change for a sample of lac lake on hydrated alumina in the different media studied. As described above, the watercolour wash fades most rapidly, followed by the sample in egg tempera. The samples in dense watercolour and in oil fade most slowly. The errors in measuring these two particularly dark samples of pure lake pigment are apparent in this figure.

It appears, therefore, that if the pigment is applied in a dense layer and properly bound in and wetted by sufficient medium, it will initially survive far better than when thinly painted, or bound in insufficient
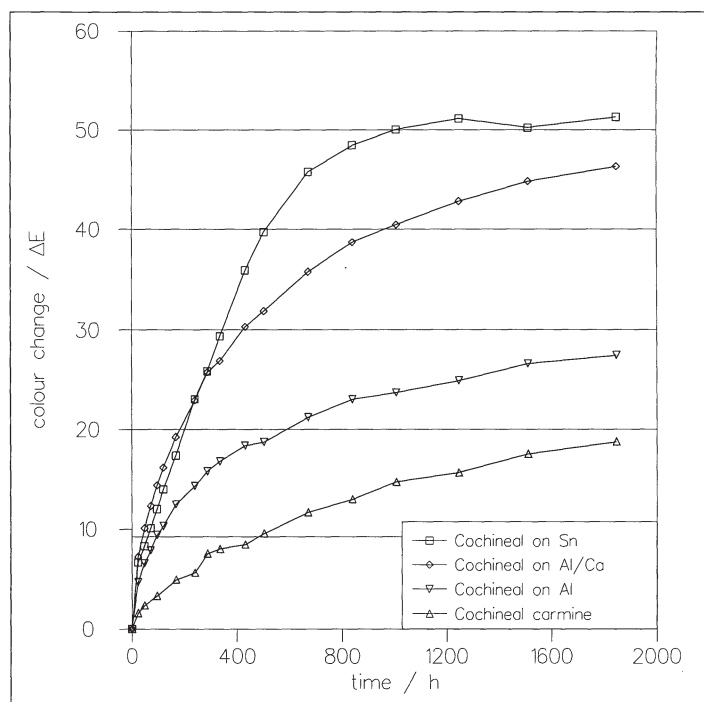

Fig. 9 Colour change against time for cochineal lake pigments on three different substrates (aluminium-containing, calcium/aluminium-containing, and tin(IV) oxide) and for cochineal carmine, all painted out as watercolour washes.
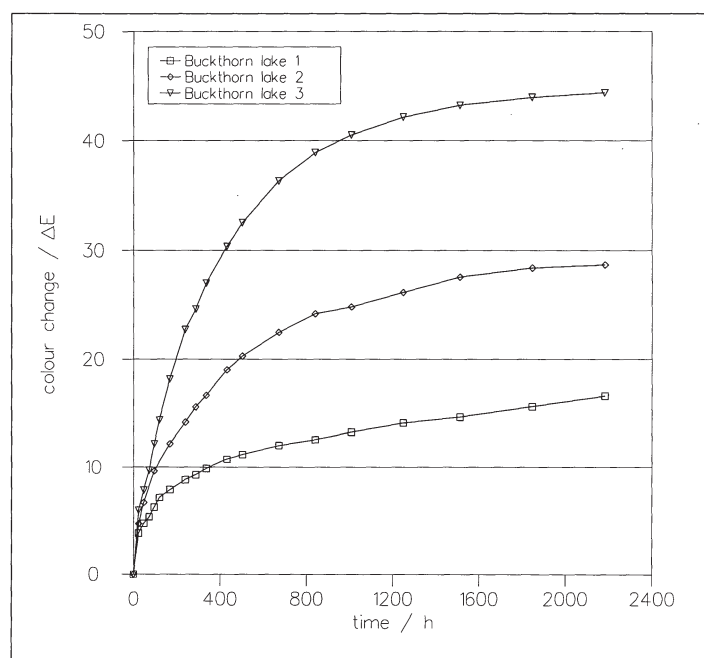

Fig. 10 Colour change against time for buckthorn lake pigments on three different substrates painted out as watercolour washes (see text).
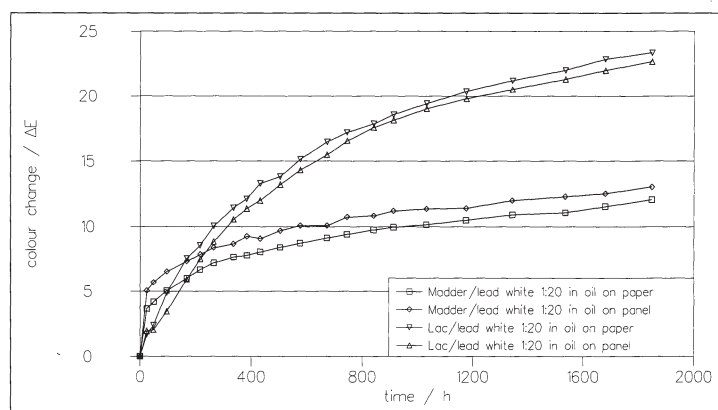
Fig. 11 Colour change against time for mixtures of madder or lac lake with lead white (ratio 1:20) painted out in oil medium on two different substrates.
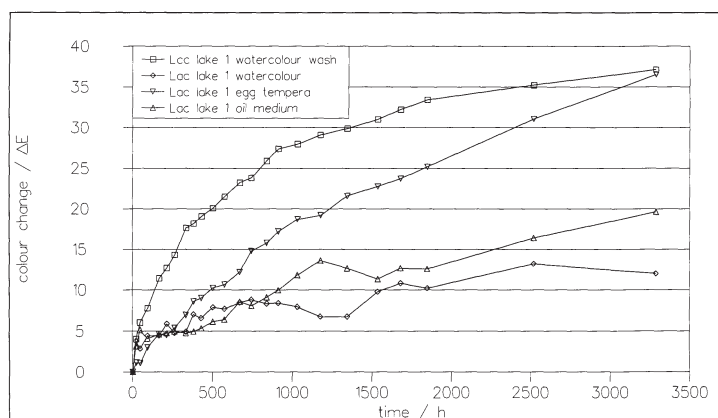

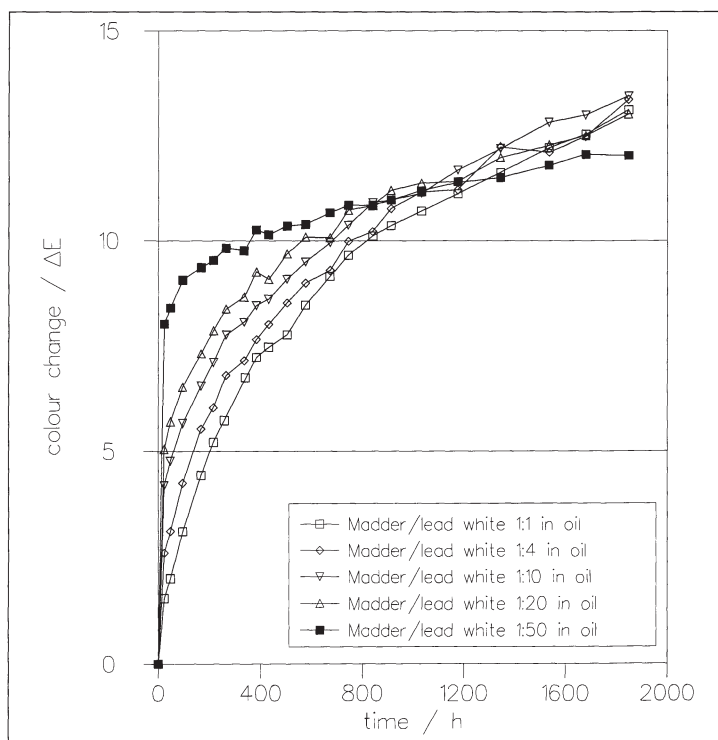**Fig. 12** Colour change against time for lac lake painted out in different media.

Fig. 13 Colour change against time for mixtures of madder lake with lead white in different ratios painted out in oil medium.

medium. The protective effect of a concentrated solution of gum arabic in a strongly pigmented film is, perhaps surprisingly, equivalent to that of linseed oil, at this early stage in the life of the paint film at least. The egg tempera paint tested, although applied as densely as the thick watercolour layer, was a rather leaner paint: it faded more rapidly. Eventually, even the oil-bound films lose colour in an analogous manner to the samples in watercolour wash and egg tempera, but because of the enhanced protection provided by the oil medium this will take very much longer.[48]

Both egg tempera and gum arabic films dry essentially by evaporation of the water present; drying of an oil film is, however, a chemical process in which the glyceride molecules of the oil are polymerised (linkage being through the constituent polyunsaturated fatty acids) by a free radical chain reaction. While initially the effect of a lake pigment on the oil film is to impede its drying (presumably by removal of the alkoxy or peroxy radicals formed during the polymerisation process), a very much longer term effect may be to speed up those processes causing the ultimate degradation of the film.[49]

Each of the samples in oil medium shows an initial colour change due in part to the bleaching of the oil film: this effect can be seen in the curve for a sample of lac lake in oil medium in Fig. 12 and more dramatically in Fig. 13, as discussed below. In addition to the bleaching, there may be a small initial colour change due to a slight rise in temperature, but an analysis of the changes in a* and b* gave no further insight into the nature of this effect.

The effect of white content
It is apparent that the higher the proportion of lead white added to the lake pigment, the greater the initial change in colour. This is illustrated in Fig. 13, which shows the colour change for a series of madder lake/lead white mixtures in oil medium.

The initial change in colour can, however, be attributed largely to a loss of yellowness in the oil medium, which is most obvious in the samples which contain the highest proportion of lead white. Fig. 14 is a graph of L* against b* for three of the madder/lead white mixtures shown in Fig. 13. During the first measurement period (about 24 hours) the main colour changes are, indeed, decreases in yellowness (b*). Thereafter the yellowness, lightness and redness (not shown) all decrease in concert.

The initial colour change is greater in comparable samples in egg tempera, probably due to bleaching of the colorants in the egg yolk. Again the decrease in yellowness is most apparent in those samples which contain a high proportion of lead white. In the equivalent samples in dense watercolour medium there is only a small colour change

during the first measurement period: gum arabic is not markedly coloured.

Once the initial colour change has occurred, the rate of change of colour is similar, regardless of the medium or the proportion of white, until the concentration of colorant becomes very small. In this study and throughout the experiments described, no attempt has been made to measure the rate of pigment loss rather than the rate of change of visual appearance.[50]

A comparison of the colour difference between a series of lac lake/lead white mixtures reveals that the gradation of shades is altered by the fading process. The table below indicates the colour difference (ΔE) between successive tints after 24 hours (to allow for the initial colour change) and after about 2200 hours.

| Time (hours) | Colour difference ΔE | | | |
| | Step in lac lake : lead white ratio | | | |
	from 1:1 to 1:4	from 1:4 to 1:10	from 1:10 to 1:20	from 1:20 to 1:50
24	12.81	13.28	13.77	12.80
2200	22.01	18.31	6.10	5.50

It can be seen that at the beginning of the experiment the visual difference between successive tints is quite similar ($\Delta E = 13.3 \pm 0.5$). After fading the colour difference between the three lightest tones is considerably reduced, while the difference between these and the deeper tones has increased (see Plate 5). This corresponds to the phenomenon seen in paintings, in which there is an accentuation of the depth of shadows and a loss of modelling in the mid to light tints. This may be attributed to a more pronounced loss of colour in the paler areas than in the dark tones of the same pigment in shadows or folds.

It has also been demonstrated that above a certain pigment concentration in mixtures with white or in glazes, there is an initial increase in chroma or saturation of the colour as fading proceeds, which might also further exaggerate the modelling.[51]

The effect of ultra-violet filtration

It has been demonstrated that the rate of fading of certain pigments can be reduced by excluding ultra-violet radiation of wavelengths below 400 nm from the illumination.[52] The light source used in the fading chamber contains a comparable proportion of ultra-violet radiation to average daylight. When the pigments examined in the study were protected by an ultra-violet filter there was a slight decrease in the rate of colour change. The effect of an ultra-violet filter upon the rate of fading of two representative pigments in watercolour wash is shown in Fig. 15.

One effect of the choice of lead white is that ultra-violet radiation entering the paint layer is not absorbed by the white pigment as would be the case
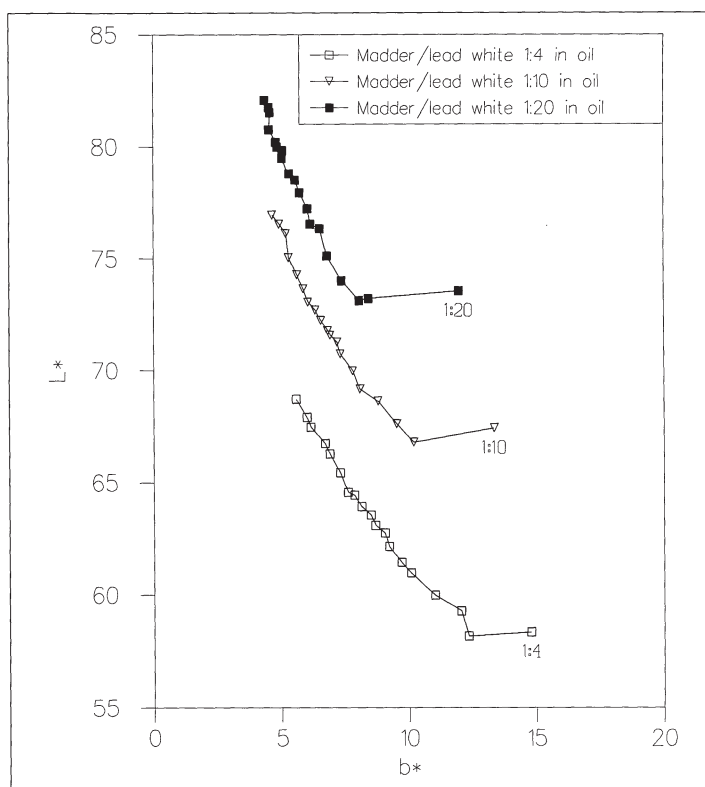
Fig. 14 Changes in lightness (L^*) and yellowness (b^*) on exposure to light for mixtures of madder lake with lead white in different ratios painted out in oil medium. The labels are adjacent to the points representing the colour of each sample before light exposure.
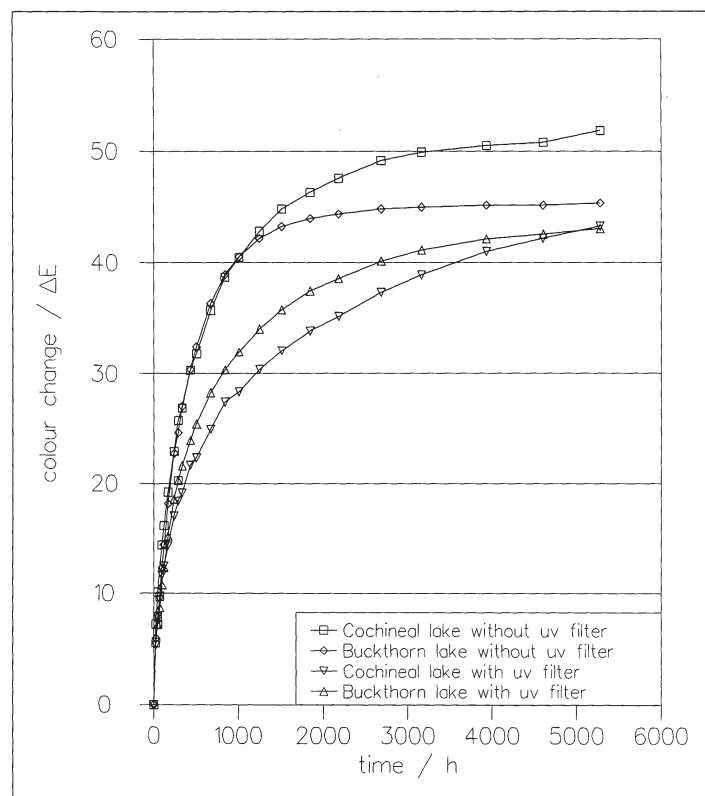
Fig. 15 Colour change against time for cochineal and buckthorn lake pigments on calcium/aluminium-containing substrates painted out as watercolour washes. The effect of an ultra-violet filter on the rate of colour change.

Plate 5 Lac lake, alone and mixed with lead white in proportions from 1:1 to 1:50 (w:w), in egg tempera: (below) control panel and (above) panel exposed to light, photographed after 2200 hours.

with titanium white.[53] Reflection of ultra-violet radiation within a lead white-containing paint layer might, thus, cause rather more colour change than if TiO_2 had been chosen.

Conclusions

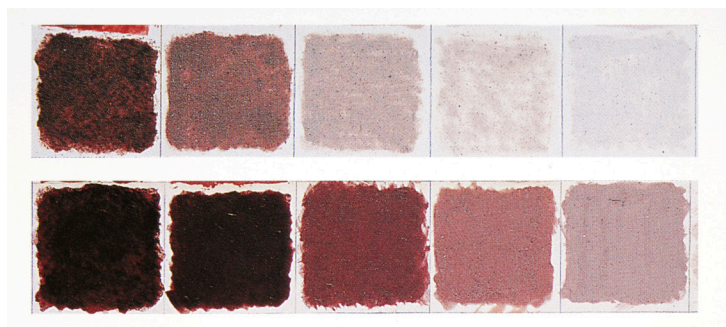Of the red lake pigments studied, those derived from scale insect dyestuffs are more fugitive than those obtained from madder. These findings are in accordance with the comments made by late eighteenth-century and early nineteenth-century writers, who recommended madder lakes as being the more permanent.[54] There is little evidence that madder lakes were readily available to Reynolds and his contemporaries during the eighteenth century. Bearing in mind Mason's comment (see p. 79), it is just as well that Reynolds does not seem to have used brasilwood lakes (which were, in fact, more often used as decorators' pigments), given their extremely fugitive nature and the unpleasant brown shade they acquire during fading.

The above results would not necessarily have been anticipated from studies of the fading of the same dyestuffs on textiles: cochineal dyed on wool or silk, even with an alum mordant, apparently has a lightfastness as good as, or better than, that of madder.[55] In the study described in this article, a sample of cochineal dyed on wool, using an alum and cream of tartar mordant, was found to be considerably more lightfast than any of the cochineal lakes tested. Weld dyed similarly on wool was slightly more lightfast than the weld lake on hydrated alumina. This suggests that in these cases the dyestuff/mordant/fibre system may be rather more lightfast than the dyestuff/substrate system.

Alizarin crimson, which is among the most fugitive of present-day pigments, is more permanent than any of the pigments prepared from naturally occurring dyestuffs tested; alizarin is one of the principal constituents of madder dyestuff, from which the most permanent lakes were prepared.

In the lake pigments tested, it appears that those prepared indirectly by extraction from cloth shearings are rather less lightfast than the equivalent lakes

prepared directly from the raw materials. The extraction procedure used in the laboratory in this study was relatively gentle, perhaps rather more so than that used in the past. As this method was used to prepare lakes from very expensive dyestuffs for over two hundred years, the pigments must have been of acceptable quality.

In the red and yellow pigments tested, those with hydrated alumina as substrate were more lightfast than those with substrates containing aluminium and calcium. Yellow pigments containing the latter substrate fade very rapidly indeed. Since the resulting colour was lighter and of higher chroma, yellow lake pigments were frequently prepared on substrates of this type (or on naturally occurring chalk-containing earths, which would presumably behave similarly). It may be that many of these, like the sample from the Cuyp painting (Plate 4), have faded. As the calcium-containing part of the substrate can be added until the desired tint is obtained, excess substrate may easily be present. This will act as an extender which may improve the working properties of the pigment, but will also have a detrimental effect on its permanence. The cochineal lake on tin(IV) oxide was the most fugitive of all the cochineal lakes tested (no cochineal lake prepared using chlorides of tin was tested). Carmine prepared according to an early nineteenth-century recipe was more permanent to light than any of the cochineal lakes.

The medium appears to offer some protection from colour change in the early stages of light exposure, provided that the pigment particles are sufficiently well bound. The leaner the paint, the less the protection. Thus, for paint films of similar pigment density, egg tempera was found to be less efficient than oil at protecting the pigments from fading, under these experimental conditions. In watercolour wash both red and yellow lakes fade very rapidly. Although the densely pigmented watercolour samples, rich in medium, initially fade no faster than those in oil medium, the paint layer becomes cracked and unstable. In practice gum arabic medium would not be used in this manner.

If the lake pigment is used in a glaze, unmixed with

white, the greater the pigment density and the thicker the layer, the more likely the colour is to survive. This effect is seen in the well-preserved coloured shadows of Christ's robe in the San Pier Maggiore Altarpiece, Plate 2. Similarly, among textile dyestuffs, it has been found that lightfastness increases with colorant concentration.[56]

After any rapid decrease in yellowness of the medium, the initial rate of change of colour of the tints of the lake pigments with white does not seem to depend markedly on the proportion of the pigments. As a result, the difference between the colorant concentration in the lightest tints decreases quite rapidly, as seen in Plate 5. In paintings, the loss of modelling which results can be seen in, for example, the Virgin's robe in *The Virgin and Child before a Firescreen*, Plate 1, p. 20.

It is known that larger particles of an organic pigment exhibit better lightfastness than smaller particles, presumably because of the relatively greater surface area in the latter. In cross-sections, it is not uncommon to find that one or two large coloured particles of lake survive at the bottom of paint layers of samples taken

from faded areas, exactly as described for the paint of the Countess of Albemarle's face (Plate 1).[57]

Finally, there is strong evidence that the exclusion of ultra-violet radiation decreases the rate of colour change in these rather fugitive organic colorants. To preserve the lake pigments in their present condition and to minimise future damage it is clearly important to limit visible light exposure and eliminate ultra-violet radiation in exhibition areas.

Acknowledgements

Note

Some preliminary results from this study were presented at the 11th annual meeting on Dyes in History and Archaeology held in York, November 1992.

Notes and references

1. M. Davies, *The British School*, National Gallery Catalogues, 2nd edn. (revised), London 1959, pp. 83–4.
2. N. Penny, ed., *Reynolds*, exhibition catalogue, Paris/London 1985–6, pp. 194–5.
3. See, for example, M.K. Talley, '"All Good Pictures Crack": Sir Joshua Reynolds's practice and studio', in Penny, op. cit., pp. 55, 64–6. For the pigments used by Reynolds for painting flesh around 1755, including both lake and carmine, see J. Northcote, *The Life of Sir Joshua Reynolds . . . and a Brief Analysis of his Discourses*, 2nd edn., London 1818, Vol. 1, p. 78.
4. W. Mason, 'Anecdotes of Sir Joshua Reynolds, chiefly relative to his manner of coloring', *Sir Joshua Reynolds' Notes and Observations on Pictures, chiefly of the Venetian School . . .*, ed. W. Cotton, London 1859, pp. 51–2.
5. D. Bomford, A. Roy and D. Saunders, 'Gainsborough's "Dr Ralph Schomberg"', *National Gallery Technical Bulletin*, 12, 1988, pp. 44–57.
6. For the discussion of lake pigments, used alone and mixed with blue, and illustration of the principal panels of the San Pier Maggiore altarpiece see D. Bomford, J. Dunkerton, D. Gordon and A. Roy, *Art in the Making: Italian Painting before 1400*, exhibition catalogue, London 1989, plate 142, p. 161, and pp. 179–80. See also M. Davies, *The Early Italian Schools*, revised by D. Gordon, National Gallery Catalogues, London 1988, pp. 45–54 for the identification of saints.
7. Mixtures of azurite and an unidentified red lake pigment have been found in the robes of several saints in the Santa Croce Altarpiece: see Bomford *et al.*, op. cit., p. 119; plate 103, p. 120; plates 106–7, pp. 121–2, and plate 122, p. 123.
8. See the article on *The Virgin and Child before a Firescreen* in this *Bulletin*.
9. A. Burnstock, 'The Fading of the Virgin's Robe in Lorenzo Monaco's "Coronation of the Virgin"', *National Gallery Technical Bulletin*, 12, 1988, pp. 58–65.
10. C. Villers and G. Hedley, 'Evaluating Colour Change: Intention, Interpretation and Lighting', *Lighting: Preprint of a Conference on Lighting in Museums, Galleries and Historic Houses*, organised by the Museums Association, United Kingdom Institute for Conservation and the Group of Designers and Interpreters in Museums, Bristol 1987, pp. 17–24.
11. J.-F.-L. Mérimée, *De la peinture à l'huile*, Paris 1830 (facsimile reprint, Puteaux 1981), p. 144: 'Les laques jaunes ont en général peu de solidité: aussi voit-on, dans plusieurs tableaux flamands, des feuilles d'arbres devenues bleues, parce que la laque jaune, mêlée à l'outremer, a disparu.'
12. See the article 'Rembrandt and his Circle: Seventeenth-century Dutch Paint Media Re-examined' in this *Bulletin*.
13. M. Davies, *The French School*, National Gallery Catalogues, London 1946, p. 53.
14. N. MacLaren, *The Dutch School 1600–1900*, revised by C. Brown, National Gallery Catalogues, London 1991, pp. 86–7, 91–2.
15. Elemental mapping of the layer indicated the presence of silicon, with traces of potassium, aluminium, magnesium and other elements. The paint layer appeared to contain several large particles in which calcium was the predominant element, in a 'matrix' of the other elements. Thanks are due to Marika Spring who carried out the examination of the painting and the preparation and analysis of this sample. See also M. Wyld, J. Mills and J. Plesters, 'Some Observations on Blanching (with

Special Reference to the Paintings of Claude)', *National Gallery Technical Bulletin*, 4, 1980, pp. 61–2.

16. Villers and Hedley, op. cit. (note 10).

17. Early research on textile dyestuffs is summarised by Padfield and Landi, cited below; see also C.H. Giles and R.B. McKay, 'The Lightfastness of Dyes: a Review', *Textile Research Journal*, 33, 7, 1963, pp. 527–77, especially pp. 528–9.

18. T. Padfield and S. Landi, 'The light-fastness of the Natural Dyes', *Studies in Conservation*, 11, 1966, pp. 181–96.

19. See, for example, D.G. Duff, R.S. Sinclair and D. Stirling, 'Light-induced Colour Changes of Natural Dyes', *Studies in Conservation*, 22, 1977, pp. 161–9; B.L. Ford, 'Monitoring Colour Change in Textiles on Display', *Studies in Conservation*, 37, 1992, pp. 1–11.

20. P. Cox Crews, 'The Fading Rates of Some Natural Dyes', *Studies in Conservation*, 32, 1987, pp. 65–72; G.S. Egerton and A.G. Morgan, 'The Photochemistry of Dyes. II – Some Aspects of the Fading Process', *Journal of the Society of Dyers and Colourists*, 86, 1970, pp. 242–9.

21. G. Field, *Examples and Anecdotes of Pigments. Practical Journal 1809*, f. 300v. Field Manuscripts, Field/6, photographic copy, Courtauld Institute Library, London. For a discussion of Field's work see R.D. Harley, 'Field's manuscripts: Early Nineteenth Century Colour Samples and Fading Tests', *Studies in Conservation*, 24, 1979, pp. 75–84; Field's description of how he set up his experiments is quoted on p. 77.

22. Field, op. cit., ff. 311, 330, 355, 372 (carmines); 314, 331–2, 355 (Indian or lac lakes); 332 (kermes lakes). Field wrote: 'I question these being true Kermes lakes', but their properties as described are what might be expected for kermes lakes. He found them to be rather less fugitive than cochineal lake.

23. Much of the nineteenth-century work, including the Russell and Abney report, is summarised by A.H. Church in *The Chemistry of Paints and Painting*, 3rd edn., London 1901, pp. 325–48.

24. W.J. Russell and W. de W. Abney, *Report to the Science and Art Department of the Committee of Council on Education on the Action of Light on Watercolours*, London 1888. The results are summarised in N.S. Brommelle, 'The Russell and Abney Report on the Action of Light on Water Colours', *Studies in Conservation*, 9, 1964, pp. 140–52.

25. V. Vesce, 'Exposure Studies of Organic Pigments in Paint Systems', *Official Digest*, December 1959, Part 2, pp. 1–143.

26. H.W. Levison, *Artists' Pigments: Lightfastness Tests and Ratings*, Hallandale, Florida, 1976.

27. A recent review of the effect of gaseous pollutants on organic dyestuffs and pigments is given in L.G. Salmon and G.R. Cass, 'The Fading of Artists' Colorants by Exposure to Atmospheric Nitric Acid', *Studies in Conservation*, 38, 1993, pp. 73–91 and the references therein; see also M. Saito, C. Minemura, N. Nanashima and M. Kashiwagi, 'Color Fading Behaviour of Anthraquinone Dyes due to Environmental Conditions', *Textile Research Journal*, 58, 8, 1988, pp. 450–4; C.H. Giles, R. Haslam and D.G. Duff, 'An Examination of the Cause of the Humidity Sensitivity of the Lightfastness of Dyed Materials', *Textile Research Journal*, 46, 1, 1976, pp. 51–4.

28. This work is summarised in R.M. Johnston-Feller, 'Reflections on the Phenomenon of Fading', *Journal of Coatings Technology*, 58, 1986, pp. 33–50.

29. Vesce, op. cit., pp. 19, 27–8, 30–1, and Tables 29–41 and 52, pp. 85–97, 108; on soluble azo reds and alizarin lake in particular.

30. P. Cox Crews, 'The Influence of Mordant on the Lightfastness of Yellow Natural Dyes', *Journal of the American Institute for Conservation*, 21, 2, 1982, pp. 43–58.

31. J. Kirby, 'The preparation of early lake pigments: a survey', *Dyes on Historical and Archaeological Textiles*, 6, 1987, pp. 12–18.

32. See, for example, G. Rosetti, [*Plictho de larte de tentori*] *The Plictho of Gioanventura Rosetti*, trs. S.M. Edelstein and H.C. Borghetty, Cambridge, Mass., and London 1969 (includes facsimile of 1st edn., Venice 1548); 'Tbouck van wondre', in *Middelnederlandse verfrecepten voor miniaturen en "alderhande substancien"*, ed. W.L. Braekman, Brussels 1986 (SCRIPTA Mediaeval and Renaissance Texts and Studies, Vol. 18, published by the Research Center of Mediaeval and Renaissance Studies, Brussels; 1st edn., Brussels 1513).

33. Whatman Silversafe paper (supplied by Atlantis Fine Art and Archival Suppliers, London) was originally designed for use in the conservation of photographs. It is a 100% cotton fibre paper sized with a neutral ketene dimer, which forms a hydrophobic ester on the surface of the paper. It is unbuffered and has a pH of 6.

34. J.S. Mills and R. White, *The Organic Chemistry of Museum Objects*, London 1987, pp. 30–4.

35. The transmittance curve for this material can be found in D. Saunders, 'Ultra-Violet Filters for Artificial Light Sources', *National Gallery Technical Bulletin*, 13, 1989, pp. 61–8.

36. Blue wool standards numbers 1 to 3, which comply with British Standard 1006:1978 (Colour Fastness to Light), were supplied by the British Standards Institution, Manchester.

37. The use of the Minolta CR200 meter to measure the colour of samples of textiles is described in Ford, op. cit. (note 19), pp. 2–3.

38. Commission Internationale de l'Eclairage, 'Recommendations on uniform color spaces, color difference equations, psychometric color terms', Supplement No.2 to *CIE Publication No.15 (E-2.3.1), 1971/(TC-1.3)*, 1978.

39. F.J.J. Clarke, R. McDonald and B. Rigg, 'Modification to the JCP79 Colour-Difference Formula', *Journal of the Society of Dyers and Colourists*, 100, 1984, pp. 128–32.

40. Mills and White, op.cit. (note 34), p. 34; Levison, op. cit. (note 26), pp. 27–30.

41. The lightfastness of anthraquinones is said to decrease as the number of -OH substituents in the molecule increases, for example: see Egerton and Morgan, op. cit. (note 20), p. 247. This is, however, only one of several factors affecting stability of the molecule to light: see H.C.A. van Beek and P.M. Heertjes, 'Fading by Light of Organic Dyes on Textiles and Other Materials', *Studies in Conservation*, 11, 3, 1966, pp. 123–32; H. Zollinger, *Color Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments*, New York 1987, pp. 251–60 (largely concerned with synthetic dyestuffs).

42. For the structure of brazilein and the flavonoid dyestuffs see *The Flavonoids*, ed. J.B. Harborne, T.J. Mabry and H. Mabry, London 1975; for the anthraquinone dyestuffs see R.H. Thomson, *Naturally Occurring Quinones*, 2nd edn., London 1971.

43. The relative permanence of weld lake by comparison with similar yellows was noted by Mérimée, op. cit. (note 11), p. 120; as a textile colorant, weld is also the most permanent of the natural yellow dyestuffs: see Padfield and Landi, op. cit. (note 18), p. 186; Cox Crews 1987, op. cit. (note 20), pp. 68, 70.

44. For the formation of a yellow intermediate compound during the fading of alizarin crimson see R.M. Johnston-Feller, R.L. Feller, C.W. Bailie and M. Curran, 'The Kinetics of Fading: Opaque Paint Films pigmented with Alizarin Lake and Titanium Dioxide', *Journal of the American Institute for Conservation*, 23, 1984, pp. 114–29; see also Johnston-Feller 1986, op. cit. (note 28), pp. 37–9. In the natural anthraquinone dyestuffs, the position is rendered considerably more complicated by the fact that each contains more than one component; some of these minor components (flavokermesic acid, for example) are yellow: see J. Wouters and A. Verhecken, 'The Scale Insect Dyes (*Homoptera: Coccoidea*). Species Recognition by HPLC and Diode-Array Analysis of the Dyestuffs', *Annales de la Société entomologique de France*, n.s. 25, 4, 1989, pp. 393–410. The dyestuff extracted from madder (*Rubia tinctorum* L.) is known to contain 23 hydroxyanthraquinone constituents, many of which are yellow, although most are present in very small quantity; see H. Schweppe, 'Identification of Red Madder and Insect Dyes by Thin-Layer Chromatography', *Historic Textile and Paper Materials II: Conservation and Characterisation*, American Chemical Society Symposium series no. 410, Washington 1989, pp. 190–3. An appreciable fading of these relative to the (major) red constituents would contribute to the observed loss of yellowness.

45. Analysis of the two kermes lakes by high-performance liquid chromatography suggests that the proportion of flavokermesic acid present is higher in the lake prepared by direct extraction from the scale insect than in that prepared from wool clippings. The madder lake obtained using the dyestuff extracted from wool clippings was found to contain less alizarin than the lake prepared by direct extraction of the dyestuff. There is some evidence that the uptake of alizarin during madder dyeing occurs later in the dyeing process than that of the more water-soluble purpurin. This could be a factor affecting the nature of the dyestuff available for pigment preparation, even before any extraction from the wool takes place: see G.W. Taylor, 'The Chemistry of Madder Dyeings: The Application of Semi-Quantitative TLC', *Dyes in History and Archaeology*, 10, 1991, pp. 35–7.

46. For a discussion of different dyeing methods related to the strength of the cochineal-mordant-fibre bonds, see V.P. Golikov, 'Technology of Dyeing Silk by Cochineal. Part 1. Theoretical Analysis of the Problem and Development of Investigation Methods', *Preprints of the International Council of Museums Committee for Conservation*, 9th triennial meeting, Dresden 1990, pp. 289–93.

47. This should be compared with the behaviour of the same dyestuffs on textiles with different mordants, remembering that the tin salts used would be in the form of tin(II) chloride, not tin(IV) oxide: see Padfield and Landi, op. cit. (note 18), pp. 183–9; cochineal (and all the scale insect dyestuffs) are more lightfast when dyed using a tin-containing mordant than with an aluminium-containing mordant. Cox Crews 1982, op. cit. (note 30), discusses the effect of different mordants, although not in the context of these dyestuffs. A calcium salt might be added to the dyebath to improve the colour of certain dyestuffs such as madder or weld, but calcium salts were not used as mordants, strictly speaking.

48. In another experiment, a sample of buckthorn lake painted out as a thin transparent glaze over lead white faded in a manner comparable with buckthorn lakes in watercolour and egg tempera, but more slowly.

49. Mills and White, op. cit. (note 34), pp. 30–3. The authors are grateful to Raymond White for further useful discussions on this point. Under normal circumstances, complete hardening of an egg tempera film may take several months, depending on the ambient conditions; it takes many, many years for complete polymerisation of an oil film to take place.

50. The rate of pigment loss in alizarin crimson/titanium white mixtures is discussed by Johnston-Feller et al., op. cit. (note 44); see p. 126 for curves of rate of colour change.

51. R.M. Johnston-Feller and C.W. Bailie, 'An Analysis of the Optics of Paint Glazes: Fading', *Science and Technology in the Service of Conservation; Preprints of the Contributions to the IIC Washington Congress, 3–9 September 1982*, ed. N.S. Brommelle and G. Thomson, London 1982, pp. 180–4; see also Johnston-Feller 1986, op. cit. (note 28), pp. 45–9, esp. fig. 29, p. 48.

52. D. Saunders, 'New Ultra-Violet Filters for Museums and Galleries', *Preprints of the CIBSE National Lighting Conference*, Cambridge 1990, pp. 308–22.

53. E.J. Dunn, 'White Hiding Lead Pigments', *Pigment Handbook*, ed. T.C. Patton, New York 1973, Vol. 1, pp. 65–75, esp. p. 72.

54. See, for example, C. de Massoul, *A Treatise on the Art of Painting and the Composition of Colours*, London 1797, p. 208; Mérimée, op. cit (note 11), p. 144.

55. According to Cox Crews 1987, op. cit. (note 20), pp. 67–8, cochineal is the more lightfast of the two on wool, on aluminium- or tin-containing mordants; according to Padfield and Landi, op. cit. (note 18), p. 184, madder dyed on an aluminium-containing mordant is more lightfast than any of the insect dyestuffs on the same mordant.

56. Johnston-Feller 1986, op. cit. (note 28), pp. 41–3. The same effect has been observed in textile dyestuffs: see, for example Giles and McKay, op. cit. (note 17), pp. 551–3; C.H. Giles, D.J. Walsh and R.S. Sinclair, 'The Relation between Light Fastness of Colorants and their Particle Size', *Journal of the Society of Dyers and Colourists*, 93, 9, 1977, pp. 348–9.

57. O. Hafner, 'Lightfastness of Organic Pigments as a Function of Their Particle Size Distribution', *Journal of Paint Technology*, 47, 1975, pp. 64–9; Giles, Walsh and Sinclair, op. cit. (note 56), pp. 348–52. Similarly, for textile dyestuffs, see, for example, Giles and McKay, op. cit. (note 17), pp. 550–1.

Appendix: preparation of samples

Lakes prepared by direct extraction from the raw material

Cochineal lake 4a (Al substrate) [C4a][1]
Cochineal lake 5 (Al/Ca substrate) [C5][2]
Cochineal lake 8 (SnO$_2$ substrate) [C8][3]
Cochineal carmine 3b [CC3b][4]
(all from silver grain cochineal, *Dactylopius coccus* Costa, obtained from BDH, Poole, Dorset)

Kermes lake K1 [KK1][1]
(from *Kermes vermilio* Planchon, obtained from Ashill Colour Studio, Shefford, Bedfordshire)

Lac lake L1 (water extraction)
Lac lake L2 (alkali extraction) [LL2][5]
(both from stick lac, *Kerria lacca* Kerr (or a similar species), from Ashill Colour Studio)

Madder lake M1b [MM1b][4]
Madder lake M4 [MM4][4]
(both from *Rubia tinctorum* L., from Ashill Colour Studio)

Brasilwood lake Br1 [Br1][5]
Brasilwood lake Brm [BrBrm][4]
(both from Pernambuco wood, *Caesalpinia echinata*, from Ashill Colour Studio)
Alizarin Crimson
(C. Roberson & Co. Ltd: Alizarin crimson is prepared from synthetic alizarin, 1,2-dihydroxyanthraquinone, on a substrate of hydrated alumina, in the presence of sodium phosphate, a calcium salt and Turkey-red oil (sulphonated castor oil treated with ammonia or caustic soda))

Quercitron lake 1 (Al substrate) [Q1][4]
Quercitron lake 2 (Al/Ca Substrate) [Q2][4]
(both from bark of *Quercus velutina* Lam (= *Q. tinctoria* Bartr.), Baltimore, supplied by Royal Botanic Gardens, Kew)

Buckthorn lake 1 (Al substrate) [Bu1][4]
Buckthorn lake 2 (Al Substrate) [Bu2][1]
Buckthorn lake 3 (Al/Ca substrate) [Bu3][1]
(from berries of *Rhamnus infectoria* L., Smyrna, supplied by Royal Botanic Gardens, Kew)

Weld lake 1a (Al/Ca substrate) [W1a][5]
Weld lake W1 (Al substrate) [WW1][4]
(from *Reseda luteola* L., supplied by Ashill Colour Studio)

Lakes prepared by the extraction of dyestuff from dyed wool [shearings lakes][5]

Cochineal lake CD1b
(from cochineal supplied by Eliza Leadbeater, Knutsford, Cheshire)

Kermes lake KD1
Lac lake LD1
Madder lake MD4a
(all supplied by Ashill Colour Studio, as above)

The pigments were always intended for use as analytical standards, thus it was important that their composition should be known precisely. To avoid possible contamination by calcium and, in particular, iron salts, distilled water was used for all preparations. It is possible that hard water

might have given slightly different results in the case of the madder lakes.[6]

As the dyestuff content of the raw material varies, the recommended quantities of reagents were modified when necessary. Potassium carbonate was substituted for the alkali prepared from wood ash and other lyes; where no quantities or other indications were given, solutions approximating to 1–2% (w:w) K_2CO_3(aq) (0·07–0·14M approximately) were used.[7]

Lakes on a substrate of hydrated alumina were prepared by the addition of aluminium sulphate, $Al_2(SO_4)_3 \cdot 16H_2O$, or potash alum, aluminium potassium sulphate, $AlK(SO_4)_2 \cdot 12H_2O$, to a solution of the dyestuff extracted, or made alkaline, with sodium or potassium carbonate until there was no further reaction. For lakes other than those prepared from scale insect dyestuffs, the alkali might be added to the dyestuff solution containing alum, depending on the recipe.

Yellow lakes on a substrate containing hydrated alumina with calcium salt(s) were made by the addition of powdered chalk, $CaCO_3$, to a solution of the dyestuff containing alum. If the addition of chalk was halted when no further reaction occurred, calcium would be present largely in the form of calcium sulphate, $CaSO_4$. If the recipe indicated that chalk was to be added in greater quantity than would be necessary to react with the alum, unreacted chalk would be present in the substrate. The cochineal lake on a mixed substrate was prepared by adding solutions of alum in water and chalk (replacing cuttlefish bone) dissolved in dilute nitric acid to an alkaline solution of the dyestuff.

The cochineal lake on a tin substrate was prepared by the addition of tin(IV) oxide, freshly made from tin and concentrated nitric acid, washed and mixed with water, to the solution of cochineal containing a little aluminium sulphate. The resultant lake was scarlet; other recipes use tin(II) or tin(IV) chlorides to give purple lakes.

The sample of cochineal carmine used was prepared by the addition of minute amounts of cream of tartar (potassium hydrogen tartrate, $KO_2CCH(OH)CH(OH)CO_2H$) and aluminium sulphate to a dilute cochineal extract and allowing it to stand until the carmine had settled out.

The wool for the lakes prepared from clippings was $6^1/_2$ cut KB undyed, oiled, supplied by J. Hyslop Bathgate & Co., Galashiels. The oil was removed by scouring in Decon 90; it was then rinsed well. Dyeing was carried out using a mordant of 8% aluminium potassium sulphate, 7% cream of tartar.[8] The lakes were then prepared by re-extracting the dyestuff with approximately 2% K_2CO_3(aq) and precipitating the lake with alum. Complete extraction of the dyestuff from the wool was not attempted.

In early sources the precise nature of the source of lac dyestuff is not always clear; sometimes it is plain that stick lac is meant; at other times this is not so obvious. Certain eighteenth-century sources, such as the *Compendium of Colours* of 1797, describe the extraction of the dyestuff from stick lac with water, followed by evaporation of the extracted material to dryness, but no further treatment is given. For comparison with the lake prepared by alkali extraction from stick lac, a lake was prepared from the water extract obtained as described above.

Appendix notes and references

1. *Ricette per far ogni sorte di colore*; the Paduan Manuscript (Padua, Biblioteca dell' Università, Ms. 992, 17th century) in M.P. Merrifield, *Original Treatises dating from the XIIth to the XVIIIth centuries on the Arts of Painting*, London 1849 (Dover reprint, New York and London 1967), Vol. II, no. 116, pp. 702–3 (except extracted with water and alkali added thereafter) [C4a, KK1]; no. 29, p. 662 [Bu2]; no. 133, p. 708 [Bu3].

2. *A Compendium of Colors and other Materials used in the Arts dependent on Design*, London 1797, pp. 59–60 [C5].

3. L. Marcucci, *Saggio analitico-chimico sopra i colori minerali*, 2nd edn., Rome 1816, pp. 178–9 [C8].

4. P.F. Tingry, *The Painter and Colourman's Complete Guide*, 3rd edn., London 1830 (1st English edn. 1804), pp. 114 [CC3b]; pp. 120–1 [MM1b, MM4]: extraction of the dyestuff carried out in the cold; also tried gentle warming; pp. 121–2 [BrBrm, Q1, Bu1]; p. 122 [Q2]; p. 147 [WW1].

5. *Segreti per colori*; the Bolognese Manuscript (Bologna, Biblioteca dell' Università, Ms. 2681, 15th century) in M.P. Merrifield, op. cit., Vol. II, no. 129, pp. 446–7 [LL2]; no. 120, pp. 440–1 [Br1]; no. 194 'arzica', pp. 482–5 [W1a]; no. 110, pp. 432–5 [all shearings lakes].

6. It has been suggested that, as far as alizarin, the most important constituent of madder dyestuff, is concerned, the addition of an alkaline salt is necessary to enable chelation of the dyestuff molecule to the aluminium ion to take place; see E.G. Kiel and P.M. Heertjes, 'Metal Complexes of Alizarin: The Structure of Some Metal Complexes of Alizarin other than Turkey Red', *Journal of the Society of Dyers and Colourists*, 79, 1963, pp. 61–4.

7. Similar values are quoted in A. Wallert, '"Cimatura di Grana": Identification of Natural Colorants and Binding Media in Medieval Manuscript Illumination', *Zeitschrift für Kunsttechnologie und Konservierung*, 5, 1, 1991, p. 82, note 5.

8. All recipes for dyeing were taken from G. Dalby, *Natural Dyes, Fast or Fugitive*, Alcombe, Somerset, 1985.