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FRONT COVER
Garofalo, *Saint Augustine with the Holy Family and Saint Catherine of Alexandria* (NG 81), (detail of PLATE 4, p. 23).

TITLE PAGE
Garofalo, *The Virgin and Child with Saints William of Aquitaine, Clare (?), Anthony of Padua and Francis* (NG 671), (detail of PLATE 3, p. 22).

The Blackening of Vermilion: An Analytical Study of the Process in Paintings

MARIKA SPRING AND RACHEL GROUT

Introduction

The darkening of the red mercury sulphide pigment vermilion is a well-known phenomenon, but one which is not fully understood. On some paintings vermilion has survived for hundreds of years unchanged, while on others it has developed a black or silver-grey crust that can be extremely disfiguring. Some insight into the process has been gained from previous studies, which have established from experiments on test samples that various impurities can accelerate the blackening.[1] Vermilion made by the wet process, discovered in 1687, can contain impurities introduced during manufacture.[2] The dry-process vermilion and cinnabar used in earlier paintings is generally very pure, but it can still exhibit severe blackening.[3] This paper describes our investigation of the phenomenon through the detailed analysis of samples of discoloured vermilion from paintings dating from before 1687. Ten paintings in the National Gallery and two paintings from the Courtauld Gallery were studied (Table 1). They range in date from the fourteenth to the seventeenth century, and were all painted before the introduction of wet-process vermilion, so dry-process vermilion or mineral cinnabar must have been used.

Table 1. List of paintings examined

- Bernardo Daddi, *The Crucifixion and Saints* (Courtauld Gallery, Gambier-Parry bequest checklist no.82), 1348, egg tempera on panel.
- Nardo di Cione, *Saint John the Baptist with Saint John the Evangelist(?) and Saint James* (NG 581), *c.*1365, egg tempera on poplar.
- English School, *The Estouteville Triptych* (Courtauld Gallery, cat.no.109), *c.*1360–7, oil on panel.
- Attributed to Jacopo di Cione and Workshop, *San Pier Maggiore Altarpiece* (NG 569–578), 1370–1, egg tempera on poplar.
- Attributed to Niccolò di Pietro Gerini, *Triptych: The Baptism of Christ* (NG 579.1–5), probably 1387, egg tempera on panel.
- Lorenzo Monaco, *The Coronation of the Virgin* (NG 1897), probably 1407–9, egg tempera on poplar.
- Giovanni del Ponte, *The Ascension of Saint John the Evangelist, with Saints* (NG 580), probably 1410–20, egg tempera on panel.
- Paolo Uccello, *The Battle of San Romano* (NG 583), probably 1450–60, egg tempera on panel.
- Benozzo Gozzoli, *The Virgin and Child Enthroned among Angels and Saints* (NG 283), 1461–2, egg tempera on panel.
- Workshop of the Master of the Female Half-lengths, *Saint John on Patmos* (NG 717), *c.*1525–50, oil on oak.
- Jacob Jordaens, *The Holy Family and Saint John the Baptist* (NG 164), probably 1620–5, oil on oak.
- Aelbert Cuyp, *A Hilly River Landscape with a Horseman talking to a Shepherdess* (NG 53), 1655–60, oil on canvas.

Examination and analysis

The paintings examined illustrate well the unpredictable nature of the blackening of vermilion. In some paintings, such as Jacob Jordaens' *Holy Family and Saint John the Baptist* (NG 164), only a few brushstrokes of vermilion have deteriorated. The Virgin's cloak in Jordaens' painting is painted with red lake and vermilion, and some of the final strokes of vermilion, probably originally highlights, have become completely grey (plates 1 and 2). There are many areas of blackened vermilion in Uccello's *Battle of San Romano* (NG 583), such as the shafts of some of the broken lances, the legs of some of the figures in the foreground, and the

PLATE 1 Jacob Jordaens, *The Holy Family with Saint John the Baptist* (NG 164), probably 1620–5. Oak, 123 × 93.9 cm.

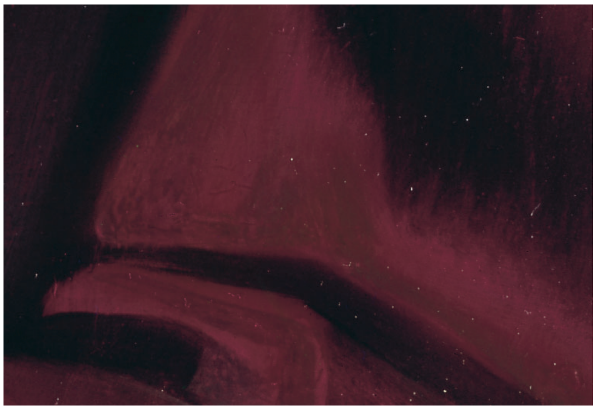


PLATE 2 Jacob Jordaens, *The Holy Family with Saint John the Baptist*. Detail of the Virgin's cloak.

PLATE 3 Paolo Uccello, *Niccolò Mauruzi da Tolentino at the Battle of San Romano* (NG 583), *c.*1440. Detail of darkened vermilion in the white charger's harness.

saddlery and harness of the white horse.[4] A border around the edge of the harness has remained red, however, as have some other seemingly random patches (PLATE 3). On many of the paintings examined only part of the modelling of a red drapery in which vermilion has been used has deteriorated. For example, in Benozzo Gozzoli's *Virgin and Child Enthroned* (NG 283), the highlights of the red drapery around the Christ Child have become completely grey while the shadows are still red (PLATE 4). Something similar can be seen on *The Ascension of Saint John the Evangelist, with Saints* (NG 580) by Giovanni del Ponte, where the blackening on Saint Jerome's red robe is not uniform, but follows the modelling (PLATE 5). Individual blackened strokes of paint can be seen next to strokes of red paint that have not deteriorated.

The appearance of the darkened paint surfaces also varies. On many of the paintings it is grey rather than black, and can have a lilac-grey colour where the deteriorated crust is thin; this is because the unchanged red vermilion below is contributing to the colour at the surface, as on the painting by Benozzo Gozzoli. In other paintings, such as Giovanni del Ponte's altarpiece of *Saint John the Evangelist*, it is a much darker grey colour.

The reason for the variation in colour became clearer when examining the surface of samples from discoloured areas under the microscope. PLATE 6 shows the surface of the sample from the painting by Benozzo Gozzoli. A crust of deteriorated pigment that consists of white, as well as black, particles has formed on the surface of the paint, beneath the varnish. Focusing through the thickness of the crust with the microscope, very thin insubstantial islands of black material can be seen lying on the surface of unchanged red vermilion, beneath bulkier white, or greyish-white, particles.

The deteriorated crust consists of both black and white material in all the paintings with darkened vermilion that were examined, a significant observation that has not been made in earlier studies. The appearance of the various samples under the microscope was remarkably consistent, differing only in the proportion of black to white material, which correlated with the appearance of the deteri-

PLATE 4 Benozzo Gozzoli, *The Virgin and Child Enthroned* (NG 283), 1461–2. Detail of the Christ Child.

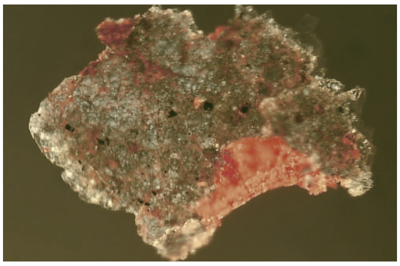
PLATE 5 Giovanni del Ponte, *The Ascension of Saint John the Evangelist, with Saints* (NG 580), probably *c.*1410–20. Detail of Saint Jerome.

oration on the painting itself. In the sample from the painting by Benozzo, there is a high proportion of white material, explaining why the deteriorated area appears purplish grey in colour. In a sample from the darker grey discoloration on the altarpiece by Giovanni del Ponte there is a higher proportion of black material in the crust although, as always, some white material is also present (PLATE 7). On the predella panel of the altarpiece of *The Baptism of Christ* by Niccolò di Pietro Gerini, the bedcover is painted with vermilion, which has discoloured to a particularly light grey colour. A high proportion of white material is visible on the surface of the sample (PLATE 8).

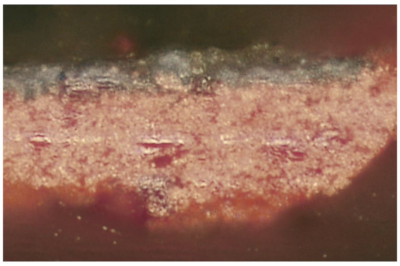
The character of the black material is especially visible in a sample from the blackened vermilion robe of one of the saints on the left panel of the *San Pier Maggiore Altarpiece* (NG 569), attributed to Jacopo di Cione and Workshop. Islands of very fine-grained black are visible on the surface of unchanged red vermilion (PLATE 9). The larger black particles that can be seen are dirt. They lie on top of the white particles, so can easily be distinguished from the black deterioration product. Although it is difficult to see any white material on the surface of this particular sample, some white particles are present and are visible in a cross-section of the sample.

PLATE 6 Benozzo Gozzoli, *The Virgin and Child Enthroned* (NG 283).

a. Detail of discoloured vermilion in the drapery around the Christ Child.



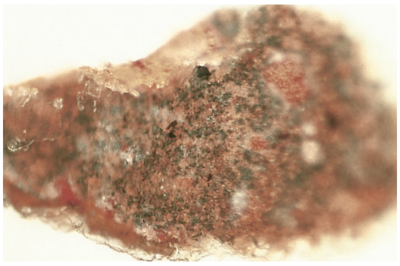
b. Surface of a paint sample from the area of discoloured vermilion. Original magnification 250×; actual magnification 110×.



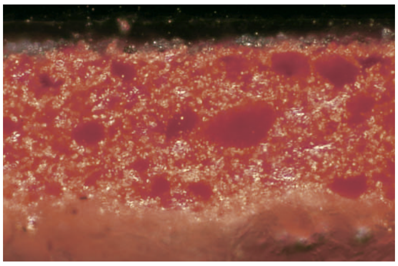
c. Cross-section of a paint sample from the area of discoloured vermilion. The grey chloride-containing crust, with unchanged red vermilion beneath it, is relatively thick. Original magnification 500×; actual magnification 450×.

PLATE 7 Giovanni del Ponte, *The Ascension of Saint John the Evangelist, with Saints* (NG 580).

a. Detail of discoloured vermilion on Saint Jerome's robe.



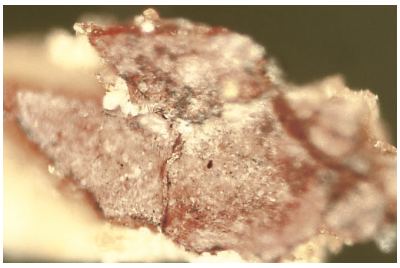
b. Surface of a paint sample from the area of discoloured vermilion. Original magnification 250×; actual magnification 160×.



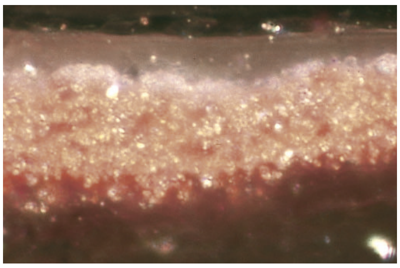
c. Cross-section of a paint sample from the area of discoloured vermilion. The grey crust on the surface of the paint is extremely thin. A few black particles are just visible beneath some white material containing chloride. Original magnification 1250×; actual magnification 560×.

PLATE 8 Niccolò di Pietro Gerini, *Triptych: The Baptism of Christ* (NG 579.1–5).

a. Detail of discoloured vermilion on the bedcover in the predella panel depicting the birth of Saint John the Baptist.



b. Surface of a paint sample from the discoloured vermilion on the bedcover. Original magnification 250×; actual magnification 160×.



c. Cross-section of a paint sample from the area of discoloured vermilion. The grey deteriorated crust on the paint surface contains a high proportion of white chloride-containing material. Original magnification 1250×; actual magnification 740×.

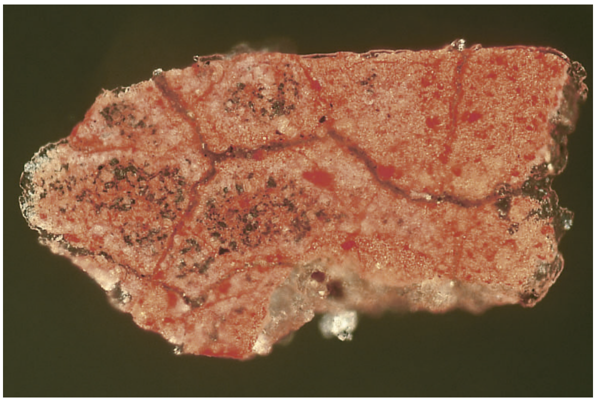


PLATE 9 Attributed to Jacopo di Cione and Workshop, *San Pier Maggiore Altarpiece*, main tier (NG 569–578), 1370–1. Surface of a sample from the discoloured vermilion robe of a saint in the left panel of the main tier. Original magnification 220×; actual magnification 170×.

The cross-sections of samples from areas of deteriorated vermilion show clearly that the deteriorated crust is extremely thin, even when the discoloration is severe enough to have a strong visual impact on the painting. In many cross-sections it is around five microns in thickness, and is barely perceptible. Some white particles, and a few black particles lying beneath the white, are just visible on the surface of the cross-section from the painting by Giovanni del Ponte (PLATE 7c), confirming what was observed in the unmounted samples.

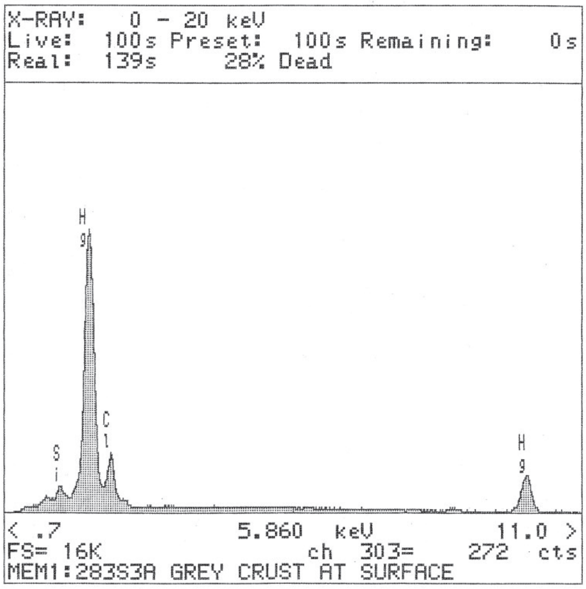


FIG. 1 EDX spectrum of a white particle in the deteriorated crust on the surface of the sample from discoloured vermilion in Benozzo Gozzoli's *Virgin and Child Enthroned*.

The crust is slightly thicker in the cross-sectionof the sample from the painting by Niccolò di Pietro Gerini. There is more white material in this sample, which forms a distinct rather crumbly and friable crust on the surface of unchanged vermilion (PLATE 8c). In this case, as in most of the cross-sections examined, the black material was too thin to be seen.

Having established that both black and white deterioration products are present, further analysis was carried out in an attempt to identify them. Spot analysis by Energy Dispersive X-ray (EDX) analysis was carried out in the scanning electron microscope, directed at a white area. In the EDX spectrum of the sample from the painting by Benozzo Gozzoli there is a very clear and clean peak for chlorine, as well as peaks that can be assigned to mercury, suggesting that a mercury chloride compound is present (FIG. 1). The detection of mercury as well as chlorine in the white particles confirms that they are a deterioration product of the vermilion, and not simply some random unrelated surface accretion. Similar EDX results were obtained for all of the paintings listed. In every case, white particles containing mercury and chlorine were found in the deteriorated crust.

Since several mercury chloride compounds are white, the next step was to try to establish which compound was present, using Raman microscopy. This technique is dependent on the behaviour of the molecule as a whole, and thus can distinguish between different compounds containing the same elements. Analysis was carried out directly on cross-sections from two of the paintings in the study, Benozzo Gozzoli's *Virgin and Child Enthroned* and the *Saint John on Patmos* (NG 717) attributed to the Workshop of the Master of the Female Half-lengths, again focusing on white particles in the grey crust on the surface of the paint. From this, the mercury chloride compound could be identified more specifically as calomel (mercury (I) chloride). FIG. 2 illustrates the Raman spectrum collected from the sample from the painting by Benozzo Gozzoli. The major peak in the spectrum from the sample, at 164 cm^{-1}, can be seen to correspond to the major peak in the standard spectrum of calomel.[5] The uppermost spectrum in FIG. 2 is that of a standard sample of vermilion, and a comparison with the spectrum from the sample shows that the small peaks are likely to be vermilion. The resolution of Raman microscopy is very good, but some of the vermilion immediately underneath the deteriorated crust may have contributed to the spectrum.

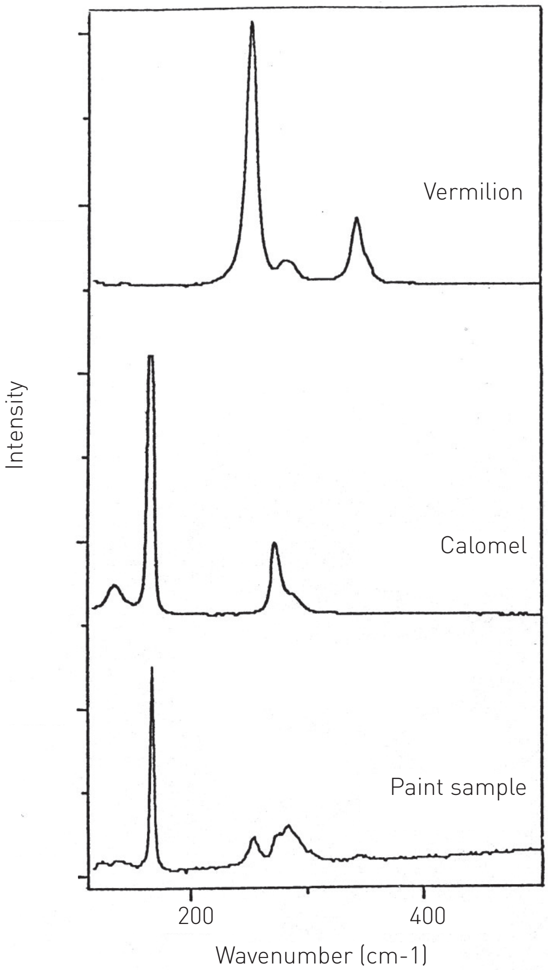


FIG. 2 Raman spectrum of a white particle in the grey deteriorated crust on the surface of a sample from an area of discoloured vermilion on Benozzo Gozzoli's *Virgin and Child Enthroned*, with spectra of standard samples of calomel (Hg_2Cl_2) and vermilion for comparison.

The black deterioration product has always been thought to be metacinnabar, the black cubic form of mercury sulphide, although this has never been convincingly proved. X-ray diffraction analysis of blackened vermilion in previous studies has given a pattern for cinnabar, but with reduced intensity relative to unblackened vermilion. It has been suggested that this may be because the black material is amorphous, or because the crystalites are too small for successful X-ray diffraction analysis.[6] With the aim of assessing the potential of Raman microscopy for the identification of metacinnabar, a spectrum of a standard sample was collected. The spectrum produced was identical to that of red vermilion, but of reduced intensity, so unfortunately it appears that Raman microscopy will not settle the question of whether the black deterioration product is metacinnabar.[7]

No chlorine was detected by EDX analysis in the unchanged particles of vermilion below the paint surface in the cross-sections. Without exception they were very pure, containing only a small amount of silicon in addition to mercury and sulphur.[8] EDX mapping of the cross-sections confirmed that the chlorine was concentrated in the deteriorated crust. Since the chlorine is present only at the surface of the sample, it must originate from an external source, the most likely being dirt. EDX analysis of dirt collected in a filter from a dirt monitor placed in Gallery 45 in the National Gallery showed the presence of chlorine, together with some sodium, which suggests that the chlorine is present as sodium chloride (FIG. 3). The sodium chloride probably originates from skin debris, since GC–MS analysis of this sample detected squalene, which is a major component of skin grease.[9] Analysis of dirt in other galleries has also shown the presence of small amounts of chloride. Gysels and Van Grieken (1999) have carried out quantitative analysis on dirt collected from three major museums, and attempted to characterise the different types of particle present in the dirt. Calcium-rich and calcium-silicon-rich particles were found in the dirt deposits collected, often with sodium chloride and sulphur adsorbed onto their surface.[10] This agrees well with the results of spot analyses of dirt collected in the National Gallery, and also explains why in some of the EDX analyses of cross-sections of discoloured vermilion, some calcium-containing particles were detected on the surface of the paint.[11]

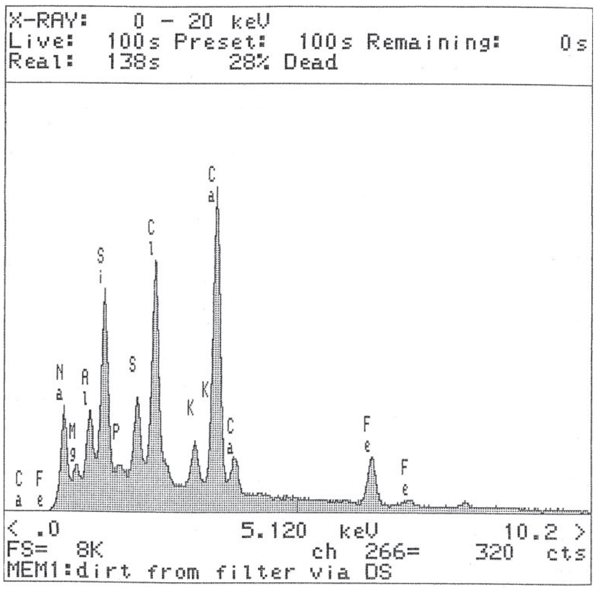


FIG. 3 EDX spectrum of dirt collected from Gallery 45.

In the case of one of the paintings studied, Uccello's *Battle of San Romano*, it can be demonstrated that the colour change of the vermilion did not happen recently, but occurred before the advent of air-conditioning and filtration of dirt in the National Gallery around the middle of the twentieth century.[12] The source of the heavy pollution for which London was notorious until the Clean Air Act of 1956 was coal burning. Some deposits of coal contain high levels of chloride ions and could release chloride into the atmosphere during combustion.[13] The results of some nineteenth-century analyses of rain water in central London, designed to measure levels of pollution, confirm that chloride was present in the atmosphere at this time.[14]

The role of chloride in the blackening of vermilion

Chloride has already been identified in previous studies as one of the ionic species that can accelerate the blackening of vermilion.[15] Vincent Daniels found that sodium chloride added to vermilion tube watercolour accelerated blackening, and that the rate of blackening increased with an increase in relative humidity.[16] A recent paper by J.K. McCormack on the darkening of mineral specimens of cinnabar also highlighted the role that chloride can play in the process. McCormack found that cinnabar from certain deposits is photosensitive (that is, it blackens in response to light), and that photosensitive cinnabar contains between 0.05% and 1% chlorine, while non-photosensitive cinnabar contains less than 0.01%. Furthermore, cinnabar from the historic sources of Monte Amiata (Italy) and Almadèn (Spain), which is not photosensitive, became photosensitive following exposure to halides.[17]

A possible mechanism for the deterioration of vermilion on paintings can be proposed from the results of McCormack's experiments to simulate the process. He found that reaction of vermilion with hydrochloric acid produced the compound corderoite ($Hg_3S_2Cl_2$). He also found that the same product was produced when vermilion was left for a long period of time in a solution of sodium chloride. It is possible, then, that sodium chloride in acidic hygroscopic dirt particles deposited on the paint surface, in a moist environment, could initiate this type of reaction on paintings. Corderoite is photosensitive and so degrades under the action of light. X-ray diffraction of the grey photodegradation product of corderoite, carried out by McCormack during his experiments, gave a pattern for calomel, an interesting result since it is the degradation product observed on paintings.[18]

Although calomel is white, the photodegradation product of the corderoite that McCormack made was dark grey in bulk appearance, so it is likely that some black material is also present which was not detectable by X-ray diffraction. Again, this is not dissimilar to what has been found in paint samples. It is possible that black mercury sulphide could be produced on the photodecomposition of corderoite. Production of calomel would involve reduction of the mercury (II) species, with concurrent oxidation, most likely of the S^{2-} ion. The fact that vermilion is a semiconductor facilitates reactivity, especially redox processes. Elemental sulphur could be produced, and, to balance the equation, mercury sulphide, which could be in the black form.

$$\underset{\text{corderoite}}{Hg_3S_2Cl_2} \xrightarrow{\text{light}} \underset{\text{calomel}}{Hg_2Cl_2} + \underset{\text{sulphur}}{S} + \underset{\text{black cubic metacinnabar or black amorphous mercury sulphide}}{HgS}$$

This reaction sequence can be summarised as initial photosensitisation of vermilion by chloride ions in a humid environment, followed by degradation by the action of light. It must be stressed that this specific proposed mechanism is speculative, but a mechanism of this type is supported by the fact that it has been shown that the light-induced darkening of vermilion pigment is faster under conditions of higher humidity.

The influence of painting technique

The main agents in the deterioration of vermilion appear to be light, humidity and certain ionic species, which in the paintings examined here has been shown to be chloride. The fact that an external agent such as chloride is involved in the deterioration process is consistent with the unpredictable behaviour of vermilion. Further understanding of this behaviour can be gained from examination of samples from blackened and unblackened areas on the same painting. The results indicate that painting technique is a key factor in determining whether the vermilion on a painting is vulnerable to discoloration.

PLATE 10 Workshop of the Master of the Female Half-lengths, *Saint John on Patmos* (NG 717), *c.*1525–50. Detail of Saint John.

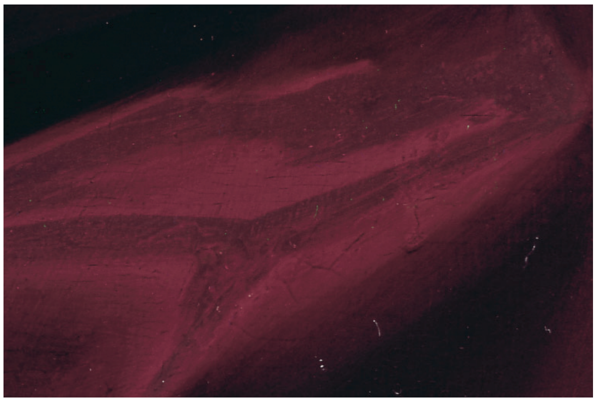


PLATE 11 Jacob Jordaens, *The Holy Family with Saint John the Baptist*. a. Detail of discoloured vermilion on the Virgin's cloak.

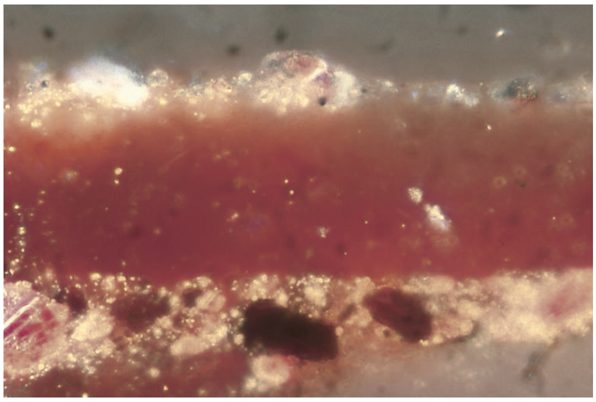


PLATE 11 b. Cross-section of a sample from the area of discoloured vermilion (PLATE 11a). White particles of mercury chloride, black particles and unchanged red particles of vermilion can be seen in the thin paint layer at the top of the cross-section. Original magnification 937×; actual magnification 590×.

In Benozzo Gozzoli's *Virgin and Child Enthroned*, the vermilion has been protected from discoloration where it has been glazed with red lake in the shadows of the drapery. R.L. Feller has already suggested that a red lake glaze over a vermilion paint will reduce the level of light to which it is exposed and filter out light of certain wavelengths, but it could also act as a physical barrier to the chloride ions.[19] Similarly the shadows of the lining of the cloak of Saint Paul on Niccolò di Pietro Gerini's *Baptism of Christ* have remained red where the vermilion has been protected by a red lake glaze applied over it. In the discoloured area vermilion was used alone, and the paint is noticeably lean and poorly bound. A sample from the undiscoloured lighter orange-red highlights showed that here the uppermost layer of paint consists of a mixture of vermilion and red lead. Samples from the undiscoloured area of Saint Jerome's robe on the painting by Giovanni del Ponte were also found to consist of vermilion mixed with some red lead; in these cases the red lead appears to have protected the vermilion from discoloration. Paint films containing vermilion are often poorly bound, and it may be that in a mixture with red lead a more coherent and resilient paint film is formed, in which the pigment is better protected from the environment by the binding medium.[20]

Vermilion seems to be particularly vulnerable to discoloration in paints where it has been used on its own. On the panel attributed to the Workshop of the Master of the Female Half-Lengths, parts of Saint John's drapery have discoloured (PLATE 10). A sample showed that in the discoloured area the uppermost paint layer consists of only vermilion bound in a drying oil. Particles of vermilion have been smeared across the resin block during grinding of the sample, suggesting that the pigment is rather weakly bound. Vermilion is known to accelerate the photo-oxidation of drying oils, which may explain the friable nature of the paint.[21] Four of the paintings that were examined were oil paintings and our results were very similar for both these and the tempera paintings. On Jordaens' *Holy Family*, another oil painting, the strokes of paint that have discoloured are extremely thin and are now rather matt in appearance. In cross-section these strokes can be seen on top of a thick layer of red lake (PLATE 11). The layer looks very friable and poorly bound, which is probably why the pigment has been vulnerable to the action of chloride ions from the environment. The vermilion coat of the horseman in Aelbert Cuyp's *Hilly River Landscape with a Horseman talking to a Shepherdess* (NG 53) has discoloured in certain areas of the modelling. In a sample from an undiscoloured area a lead-containing pigment, probably red lead, was detected in addition to vermilion, and as on tempera paintings this has resulted in a more coherent film, protecting the vermilion from deterioration.[22]

The influence of conservation history

The conservation history of a painting must also be an important factor in the discoloration of vermilion, since it determines whether the painting has been exposed to the environmental conditions that promote the colour change. It is clear that the paintings in this study have been exposed to chloride at some point in their history. Most of them have been in the National Gallery Collection since the nineteenth century, and have a reasonably well-documented conservation history from then on. The records do not reveal any direct exposure to chlorinated materials, such as their use for cleaning. The fact that chlorinated compounds have sometimes been used in air-conditioning systems as a disinfectant should also be considered but, as mentioned above, the vermilion in at least one of the paintings studied was already discoloured before the general introduction of air-conditioning.

However, many of the paintings in this study seem to have been described as very dirty at some point in the conservation records. There is also evidence from these accounts, and from examination of the surface coatings, that earlier treatments may have left the paint surfaces of some of the paintings particularly exposed to contact with dirt. The panels of the *San Pier Maggiore Altarpiece*, for example, were cleaned in the 1980s for the first time since the altarpiece entered the collection in 1857. A thin surface coating of wax polish, applied in 1953, was removed. Underneath was a yellow-grey layer of dirt, lying directly on the paint surface, suggesting that when the altarpiece was last cleaned, probably while it was in the Lombardi-Baldi collection in Florence, it was not revarnished. A detail of the left panel of the main tier during cleaning (see PLATE 12) illustrates how heavy this deposit of dirt was.[23]

Nardo di Cione's *Saint John the Baptist with Saint John the Evangelist(?) and Saint James* (NG 581) also entered the National Gallery Collection in 1857 and has a similar conservation history. The painting was cleaned in the early 1980s for the first time since 1887. The varnish that was removed during this cleaning was extremely thin, and the majority of the discoloration was attributed to grey dirt layers that had accumulated on the surface. In cross-sections taken before cleaning in the 1980s, dirt can be seen lying directly on the paint surface beneath the very thin varnish applied in 1887, suggesting that it was not thoroughly cleaned at that time.[24]

The dirt on these paintings may be responsible for the deterioration of the vermilion. As has already been mentioned, the high level of dirt in the galleries in the nineteenth century was a significant and much-discussed problem. Most of the paintings in the collection were glazed during the second half of the century to protect them from the sooty air, and remained so until after the Second World War. This measure may not have been entirely effective however, since in 1936, when Ian Rawlins examined some pictures that had been glazed, he stated that 'the amount of dust, both on the inside of the glass and on the picture itself, was extraordinarily

PLATE 12 Attributed to Jacopo di Cione and Workshop, *San Pier Maggiore Altarpiece*. Detail of the left panel of the main tier during cleaning.

large'.[25] In any case, the 'during cleaning' photographs and cross-sections taken before cleaning provide evidence that significant levels of dirt were present on the paint surfaces from the time they entered the collection until their cleaning in the 1980s.

The very thin varnish applied by Dyer on the altarpiece by Nardo di Cione was based on mastic. Several of the other paintings in the study have similar thin varnishes, also applied by Dyer in the nineteenth century.[26] Towards the end of the century, restorers employed by the Gallery were being instructed to use the whitest possible spirit varnish, thinly applied.[27] The aim was, presumably, to limit the effects of discoloration. Paintings such as Benozzo Gozzoli's *Virgin and Child Enthroned*, Niccolò di Pietro Gerini's *Baptism of Christ* and Giovanni del Ponte's *Ascension of Saint John the Evangelist, with Saints*, which still have Dyer's varnish, are not drastically discoloured – areas of white appear white rather than yellow, despite the fact that over 100 years have passed. However, it is not clear whether these thin varnishes have in fact given sufficient protection to the paint surfaces from the environment. Thin varnishes allow more light to reach the paint surface; a thick discoloured yellow varnish can act as a filter, reducing the rate of discoloration, and also acts as a physical barrier to dirt.[28] It is not known how early the discoloration occurred on the paintings that have been studied, and records of their conservation history are only available, at best, for the last century and a half. However, discussion of their history does identify factors that could put the paintings at risk to exposure to chloride, which can direct future work on possible preventive conservation measures.

Paintings from the Courtauld Gallery

In all the ten paintings from the National Gallery with severely discoloured vermilion that were examined, chloride was found to be involved in the deterioration process. Samples from two paintings from the Courtauld Gallery were also analysed to investigate whether the phenomenon extends to paintings in other collections. The paintings are listed in Table 1, p. 50. Several areas of vermilion on the central panel of a triptych by Bernardo Daddi depicting the Crucifixion have discoloured. The deteriorated areas, such as the headdress of a soldier standing to the right of the cross and the robe of the figure standing behind, have a greyish colour which is rather similar to the deteriorated areas on the National Gallery paintings. A cross-section of a sample from a discoloured area of the Magdalen's robe was examined. Both black and white material were visible on the paint surface, as in the National Gallery paintings, and again EDX analysis detected mercury and chlorine in the white material. A similar process seems therefore to have occurred on these paintings. The discoloration in the Magdalen's robe follows the modelling, and it has been found that the areas that are still red contain red lead rather than vermilion.[29]

Part of the modelling in the Magdalen's red cloak on *The Estouteville Triptych* was painted with vermilion that has now discoloured. EDX analysis established that chloride was also involved in the deterioration on this painting. The painting was in a private collection in Sussex as recently as the 1920s, and so was not exposed to the extremely polluted and dirty air of London in the nineteenth century, suggesting that central London is not the only location where chloride levels have been high enough to initiate this deterioration.[30]

Conclusion

The most important finding of this study is that in all the paintings examined the vermilion is not inherently unstable, but appears to have become so by the action of chloride ions from the environment. The mercury chloride compound formed is not a transient species, as has been suggested in earlier studies, but the white mercury (I) chloride calomel. The presence of both white and black deterioration products explains why discoloured vermilion often appears grey rather than black. Certain paintings seem to be predisposed to this type of deterioration as a result of the painting technique employed. Vermilion is vulnerable if used alone in a paint film, which explains why discoloured vermilion is most commonly observed on Early Italian paintings, particularly in the pure vermilion mid-tones of the systematically modelled draperies. The findings suggest that it is desirable to limit contact between vermilion and dirt, or other sources of chloride ions, an aim that has practical consequences for both preventive and interventive conservation procedures.[31] Some questions remain to be investigated, such as whether the involvement of chloride in the deterioration is widespread, the role of varnish in providing protection against the action of chloride, and whether the level of chloride present in today's air-conditioned galleries remains sufficient to initiate the deterioration of vermilion.

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Notes and references

1 See R.L. Feller, 'Studies on the Darkening of Vermilion by Light', *Report and Studies in the History of Art*, 1967, National Gallery of Art, Washington DC, pp. 99–111, and V. Daniels, 'The Blackening of Vermilion by Light', *Recent Advances in the Conservation and Analysis of Artifacts*, Jubilee Conservation Conference Papers, compiled by James Black, University of London, Institute of Archaeology, 1987, pp. 280–2.

2 R.J. Gettens, R.L. Feller and W.T. Chase, 'Vermilion and Cinnabar', *Artists' Pigments: A Handbook of Their History and Characteristics*, Vol. 2, ed. A. Roy, 1993, pp. 159–82. See also Feller (cited in note 1) where the work of Eibner (1914) is reviewed. Eibner showed that wet-process vermilion is less stable than dry-process vermilion, and attributed this to impurities introduced during manufacture, specifically thiosulphate.

3 Natural mineral cinnabar may sometimes have been used as a pigment in earlier paintings, although it seems likely that dry-process vermilion (made by sublimation) was much more common, because of the difficulties of obtaining cinnabar of a good colour. They are very similar microscopically, and no attempt was made to determine whether the vermilion in the samples examined was cinnabar or the dry-process form. See Gettens et al. cited in note 2.

4 A. Roy and D. Gordon, 'Uccello's *Battle of San Romano*', *National Gallery Technical Bulletin*, 22, 2001, p. 10.

5 The Raman spectrum was collected using an excitation wavelength of 784.71 nm.

6 Daniels 1987 (cited in note 1) and R. Grout and A. Burnstock, 'A study of the blackening of vermilion', *Zeitschrift für Kunsttechnologie und Konservierung*, Jahrgang 14/2000, Heft 1, pp. 15–22.

7 The Raman scattering in the spectrum of a standard sample of black metacinnabar is probably being produced from traces of hexagonal cinnabar, with cubic black metacinnabar showing no scattering. Metacinnabar should, theoretically, give an entirely different spectrum from vermilion because of its different crystal structure. See J.R. Ferraro, 'Factor Group Analysis for Some Common Minerals', *Applied Spectroscopy*, 29, No.5, 1975, pp. 418–21.

8 Quartz (SiO_2) is often found as an accessory mineral with cinnabar, but in these samples no discrete colourless particles of quartz are visible, suggesting that the silicon is contained within the structure of the mercury sulphide lattice.

9 D. Saunders, 'Pollution and the National Gallery', *National Gallery Technical Bulletin*, 21, 2000, p. 90 and p. 93, note 83.

10 K. Gysels and R. Van Grieken, 'Microanalysis of Museum Aerosols related to the conservation of works of art', *Proceedings of the 6th International Conference on 'Non-destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage'*, Rome, May 1999, Vol.1, pp. 45–62.

11 The EDX analysis was not quantitative. Some attempt was made to characterise the different particles making up the dirt by a series of spot analyses. Discrete particles of sodium chloride could be detected, as well as calcium-rich particles, calcium silicates and particles containing a combination of Ca, S, Cl and Si.

12 The blackening of the vermilion on Uccello's *Battle of San Romano* can be seen in a colour plate dating from the 1930s. See R.N.D. Wilson, *The National and Tate Galleries*, London 1930s (exact date of publication not known), plate 2. Air-conditioning was introduced to one room in the National Gallery in September 1950, followed by another six rooms in 1956. See *The National Gallery, 1938–54*, London 1955, pp. 23–4. Measurements made in 1959 showed that the air-conditioning system removed over 90% by weight of dust. The level in a naturally ventilated gallery was around 80% of that outside. The clean air act of 1956 also led to a significant reduction in the level of pollution in central London. See Saunders 2000, cited in note 9.

13 P. Brimblecombe, *Air Composition and Chemistry*, 2nd edn, Cambridge 1995, p. 110.

14 P. Brimblecombe, *The Big Smoke. A history of air pollution in London since medieval times*, Cambridge 1987, p. 146.

15 Daniels 1987, cited in note 1, refers to a number of papers by Davidson and Willsher, and Davidson et al. in which potassium iodide, chloride, bromide and fluoride, ferrocyanide, iodate, thiocyanate, cyanide and lead nitrate were found to accelerate the blackening of vermilion.

16 Daniels, cited in note 1.

17 J.K. McCormack, 'The darkening of cinnabar in sunlight', *Mineralium Deposita*, 35, 2000, pp. 796–8.

18 J.K. McCormack, personal communication.

19 Feller 1967, cited in note 1.

20 Lead could also react preferentially with chloride ions, thereby protecting the vermilion.

21 F. Rasti and G. Scott, 'The effects of some common pigments on the photo-oxidation of linseed oil-based paint media', *Studies in Conservation*, 25, 1980, pp. 145–56.

22 J. Plesters, A. Roy and D. Bomford, 'Interpretation of the magnified image of paint surfaces and samples in

terms of condition and appearance of the picture', *Science and Technology in the Service of Conservation, Preprints of the IIC Washington Congress*, September 1982, N.S. Bromelle and G. Thomson eds, London 1982, pp. 169–76.

23 J. Dunkerton, J. Kirby and R. White, 'Varnish and early Italian tempera paintings', *Cleaning, retouching and coatings, Preprints of the contributions to the Brussels IIC Congress*, September 1990, J.S. Mills and P. Smith, eds, London 1990, pp. 63–9. This paper discusses the documents that survive which record the varnishing of the *San Pier Maggiore Altarpiece* soon after it was completed. Traces of an oil/resin varnish (linseed oil plus sandarac) were found on one of the panels, which may be the remains of the original varnish. This type of varnish is likely to have provided good protection for the paint surface. It is not known when it was removed, but the painting appears to have been unvarnished when it entered the National Gallery Collection in 1857. It has long been the practice of restorers to apply the minimum amount of varnish to a painting of this period after restoration, to produce a surface of low gloss.

24 D. Gordon, D. Bomford, J. Plesters and A. Roy, 'Nardo di Cione's "Altarpiece: Three Saints"', *National Gallery Technical Bulletin*, 9, 1985, pp. 21–37.

25 Saunders 2000, cited in note 9.

26 R. White and J. Kirby, 'A Survey of Nineteenth- and early Twentieth-Century Varnish Compositions found on a selection of Paintings in the National Gallery Collection', *National Gallery Technical Bulletin*, 22, 2001, pp. 64–84. Several of the paintings discussed in this paper had varnishes applied by Dyer.

27 *An Exhibition of Cleaned Pictures (1936–1947)*, The National Gallery, London 1947, p. xvii.

28 Feller (cited in note 1) found that a yellow filter reduced the rate of discoloration of vermilion, although not as effectively as a red filter.

29 The two paintings in this study from the Courtauld Gallery are illustrated in Grout and Burnstock, cited in note 6.

30 *Catalogue of the Lee Collection,* Courtauld Institute of Art, University of London, revised edn 1962, p. 10.

31 A factor that needs to be taken into consideration during conservation treatment of paintings with severely discoloured vermilion is that the white calomel-containing material often appears to be poorly bonded to the surface of the unchanged vermilion (as seen in the cross-section from the painting by Niccolò di Pietro Gerini (PLATE 8c)) and may be vulnerable to removal during cleaning. It may be the reason for the variation in the proportion of black and white material that was observed in the deteriorated crust. It should, perhaps, also be taken into consideration that when calomel is treated with ammonia, disproportionation can occur, producing a black solid of elemental mercury and a complex mixture of mercury(II) compounds. However, whether this is a problem in practice, given that aqueous ammonia solution is usually only used in low concentration during conservation treatments, requires further investigations. See N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Oxford 1984 (1990 reprint), p. 1410.