National Gallery Technical Bulletin

Volume 19, 1998

National Gallery Publications, London
Distributed by Yale University Press

Series Editor: Ashok Roy

First published in Great Britain in 1998
by National Gallery Publications Limited
5/6 Pall Mall East, London SW1Y 5BA

British Library Cataloguing in Publication Data
A catalogue record for this journal is available from the British Library

ISBN 1 85709 220 1
ISSN 0140 7430
525270

Edited by Diana Davies and Jan Green
Designed by Helen Robertson
Origination by Jarrold Repro
Printed in Great Britain by Jarrold Book Printing

FRONT COVER:
Caravaggio, *The Supper at Emmaus*
(detail of Plate 4, p. 42)

PAGE 1:
Jan van Huysum, *Hollyhocks and Other Flowers in a Vase* (NG 1001), 1702–20. Detail.
(See Fig. 4, p. 79)

Analyses of Paint Media

BY RAYMOND WHITE, JENNIFER PILC & JO KIRBY

THE WAY in which an artist chooses to manipulate paint is inevitably closely linked to its particular physical characteristics. These include attributes like the translucency and covering power of the paint, its gloss and its drying time. Certain properties of the paint are related to its 'body': whether it gives a crisply peaked or softly rounded impasto, for example, or a thin wash. The paint may flow easily and evenly off the brush, or it may be sufficiently stiff in texture to be dragged over the layer beneath, giving a stroke of broken colour. Both pigment and binding medium contribute their particular qualities to the properties of the paint: the interaction between the two is itself an important factor, but for certain attributes, such as gloss and flow, the contribution of the paint medium is dominant.

At the time of painting, most of these features could have been readily appreciated by an observer. Inevitably, however, some of the materials used may show some alteration as they age; as a result some characteristics of the artist's work may become less clear or less comprehensible with the passage of time. If the constituents of the paint can be identified, the artist's working methods and the intended appearance of the painting may be better understood. In addition, quite subtle but deliberate modifications to the material used – a heat-bodied linseed oil rather than ordinary linseed oil, for example – may have made a marked difference to the artist's handling of the paint, to its drying time, or to its final appearance. This is particularly true of the paint medium. By the use of sensitive and sophisticated methods of analysis, in this case gas chromatography–mass spectrometry (GC–MS) and Fourier transform infra-red (FTIR)–microscopy, it has become possible to characterise minor constituents of the medium and thereby greatly to enhance our understanding of the painter's practice.

Paintings from three schools – Italian, Dutch, and nineteenth-century French (mostly by painters of the Barbizon School) – are discussed below. The analytical results obtained, summarised in the Table on pp. 87–95, illustrate most effectively how investigation of the medium may explain aspects of the artist's technique or features of the paint. Several paintings from other schools have also been examined; these are listed in the Table, but without further discussion.

Italian School paintings

Several of the Italian sixteenth-century paintings examined provide examples of common minor modifications of the paint medium to achieve a particular effect: that of gloss, richness and transparency in a glaze, providing depth and modelling to a drapery. In Francesco Bissolo's *The Virgin and Child with Saint Paul and a Female Martyr* (NG 3915), the Virgin's white headdress, the red glaze on her dress and the dark green glaze on the cloak of the female martyr on the right of the composition were all found to contain linseed oil. In the white paint this is present alone; in the two glazing colours, however, the medium has been modified by the addition of a very little pine resin. This practice appears to have been relatively common, not only in Italy but also all over Northern Europe, and has been observed in paintings dating from the fifteenth century onwards: an eighteenth-century Dutch example is discussed below. The addition of the resin raises the refractive index of the paint medium slightly so that it approaches that of the pigments – here, verdigris and a red lake pigment – resulting in a richer, more transparent glaze, as well as a glossier paint.[1] This could be achieved by the addition of a little pine resin varnish, *vernice comune*, to the oil. The sixteenth-century writer Giovanni Battista Armenini described the practice for both red lake-containing glazes and green drapery glazes and also suggested a similar addition to black (rosin soot in this case), with the comment that *vernice comune* 'is of such a quality that it gives strength and aid to all the colours that suffer on drying'. By this he probably meant that it helped to prevent them sinking, as well as giving them a fresh, glossy appearance.[2] Pine resin was indeed identified in the black background of the North Italian School picture of *Saint Hugh* (NG 692, painted between 1525 and 1600), in this case mixed with a heat-bodied walnut oil; the same oil, not heat-treated, was used for the white paint of the saint's habit. As the oils were usually heated with a drier – perhaps red

lead or lead white, umber (containing manganese) or some other material – their drying properties were enhanced; they were therefore often used with poorly drying pigments, such as black.[3] (The drying of such oils is discussed further in the section on nineteenth-century French painting.)

It should be noted that, in the green paint in Bissolo's picture, the resinous component is a simple addition to the paint medium; examination by FTIR–microscopy shows that there has been no reaction between the verdigris and the pine resin to give a 'copper resinate'. A similar use of pine resin as a minor constituent of the binding medium is seen in the uppermost glaze layers in brownish-green areas of landscape in three paintings by the Florentine artist Piero di Cosimo: *A Satyr mourning over a Nymph* (NG 698; Fig. 1), *The Fight between the Lapiths and the Centaurs* (NG 4890), perhaps dating from 1500–15, and *The Forest Fire* (Oxford, Ashmolean Museum), examined during conservation treatment carried out at the National Gallery in 1995. Walnut oil was used for the foliage examined in all three paintings, heat-prepolymerised in the first and last cases, but not in the *Fight between the Lapiths and the Centaurs*. The slightly higher refractive index of a heat-bodied oil itself results in a slightly richer, more saturated colour (even without the addition of resin), most noticeable where the pigment used has a refractive index close to that of the oil. This is true of the lake pigments and also copper salts like verdigris; such a paint gives a particularly effective deep, lustrous glaze. A prepolymerised oil also gives a smooth glossy film, without brush marks: even a little, added to paint containing ordinary oil, endows it with these characteristics. Piero was perhaps concerned with obtaining a pleasing surface finish when he chose to use a heat-bodied oil, as copper-containing green pigments dry without difficulty. The glazes are sometimes discoloured, but FTIR–microscopy shows that, as with the Bissolo, 'copper resinate' as such is not present.[4] In all three paintings, some parts of the landscape were always intended to be brown. In the *Lapiths and the Centaurs*, for example, translucent dark brown glazes were found to contain brown and black pigments as well as a copper-green pigment; browns and blacks are also present in the left foreground paint in *The Forest Fire*.[5]

A Satyr mourning over a Nymph shows an unusual drying fault. It was common practice to use a liquid drawing material to draw the composition on the prepared panel. In this painting, however, the material used for the extensive underdrawing appears to have affected the paint above, causing it to crack: the paint of the nymph's flesh, for example, shows a more marked craquelure in areas immediately above drawing than elsewhere, and the paint in areas of the sky over drawing has a reticulated appearance. The sky paint itself was found to contain walnut oil and the same medium was identified in the sky of the *Lapiths and the Centaurs* and *The Forest Fire*. FTIR–microscopy was used to examine a sample of paint from an area of the sky where the drawing was unusually substantial; this indicated the absence of lipids that might be associated with either egg tempera or drying oil in the ink layer. Traces of polysaccharide material could perhaps derive from gum and it is possible that the drawing material is an iron gall ink of some type: gum is a common ingredient, along with ground oak galls, iron (II) sulphate ($FeSO_4.7H_2O$) and perhaps a little black pigment, in water, wine or vinegar.[6] There are at least three ways in which such an ink could have affected the paint above. During the drying and cross-linking of the paint, tensions set up

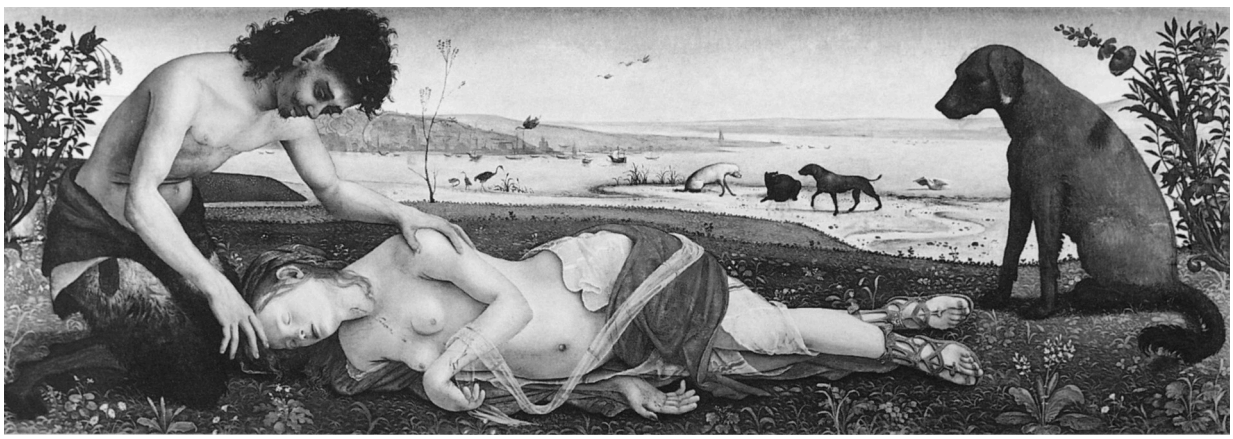

Fig. 1 Piero di Cosimo: *A Satyr mourning over a Nymph* (NG 698), *c.*1495. Poplar, 65.4 × 184.2 cm.

Fig. 2 Attributed to Sebastiano del Piombo: *Portrait of a Lady with the Attributes of Saint Agatha* (NG 24), *c.*1540. Canvas, painted area 92.4 × 75.3 cm.

would naturally be transferred to the ink layer below. If this was unusually rich in gum-like materials, which in the dried state tend to be brittle, disruption of this layer might occur; cracking of the paint would ensue. Alternatively, the ink may have been unusually acidic; its interaction with the oil medium above could similarly cause disruption to the paint. An ink rich in phenolic compounds, such as gallic acid, would inhibit the paint-drying process at the ink/oil interface, while the oil at the top of the layer would continue to dry and cross-link at the normal rate. The net result would be contraction of the paint. Heated solids probe analysis failed to resolve any residual components that might be associated with gall tannins and other constituents of an iron gall ink, and FTIR–microscopy results were not clear. However, examination of a partially hydrolysed fragment by mass spectrometry via an electrospray interface indicated the presence of galloyl-sugar residues, suggesting an ink of this type had been used.

Layers of varnish on a picture surface were difficult enough to analyse before the advent of sensitive techniques like GC–MS: unpigmented medium-rich layers occurring within the paint layer structure usually present an intractable problem. Dosso Dossi's *A Man embracing a Woman* (NG 1234), probably dated about 1524, is a fragment of a tondo thought to be from the ceiling decoration of one of a suite of rooms constructed for Alfonso d'Este in his castle at Ferrara. The history of the painting is complicated, but payments to Dosso Dossi are recorded in 1524 and 1526, including two for the purchase of ultramarine. Examination of the structure of the sky paint during conservation treatment showed that what appeared to be a natural resin varnish was present between the ultramarine-containing paint layers forming the sky and the reddish-brown paint beneath. The payments to the artist suggest that he was responsible for applying the blue paint over what appears to have been a completed, varnished, paint surface. Although the medium of the paint could be identified as walnut oil, using gas chromatography, it was not possible to identify the materials forming the varnish.[7] Recent examination of a fragment from a greenish-blue strip at the top of the painting by the more sensitive and versatile techniques of FTIR–microscopy and GC–MS has provided more information. FTIR–microscopy in transmission mode on a tiny paint fragment suggested the presence of labdane structures, indicating that a terpenoid resin other than pine was present. This was confirmed by GC–MS analysis, which revealed the presence of sandaracopimaric acid, suggesting that the resin was derived from a conifer tree within the family Cupressaceae, that is, a resin of the sandarac type. It seems from documentary sources that sandarac-type resins were commonly used in the so-called *vernice liquida*, certainly into the sixteenth century, although which genus was the source of the resin cannot be known for certain. *Tetraclinis articulata* (Vahl) Masters (true North African sandarac) or *Juniperus* spp. are most likely to have been used. Sandarac resins have rarely been identified in practice, partly because few varnish coatings observable today are this early in date, and partly because analysis of the traces that may remain has not been possible until relatively recently.[8] The survival of this example as an intermediate layer in the paint structure is extremely fortunate, from both the historical and the analytical point of view. What is known of the history of such varnishes and the documentary evidence on the painting suggests that it is contemporary and the result in effect provides further evidence supporting the identification of the picture.

An intermediate varnish layer is also present in *A Portrait of a Lady with the Attributes of Saint Agatha* (NG 24), attributed to Sebastiano del Piombo, which is thought to date from about 1540 (Fig. 2). Visual examination of the saint's attributes at the right of the painting and the martyr's palm she holds suggested

that both were painted over the brown background. Cross-sections prepared from samples of paint taken from these areas revealed the presence of a yellow-brown varnish layer above the original brown background paint. There is no indication from the pigments present at what time the repainting may have been carried out, although the presence of a mixture of lead-tin yellow and verdigris forming the green of the palm suggests that the repaint is no later than the early eighteenth century.[9] Analysis of the varnish layer by GC–MS revealed the presence of linseed oil with a conifer resin; traces of larixol indicated that a larch resin, Venice turpentine (from *Larix decidua* Miller) had been used. Documentary evidence cannot help to date the varnish in this case as Italian sources from most periods contain scattered references to the use of Venice turpentine.

The results of the examination of the medium of two paintings by the eighteenth-century Venetian painter Canaletto, *Venice: Campo S. Vidal and Santa Maria della Carità ('The Stonemason's Yard')* (NG 127), painted around 1726–30, and *Venice: The Feast Day of Saint Roch* (NG 937), of about 1735, have been reported earlier.[10] The three paintings examined recently, *Venice: The Basin of San Marco on Ascension Day* (NG 4453) and *A Regatta on the Grand Canal* (NG 4454), both dated around 1740, and *Eton College* (NG 942), of about 1754, follow the pattern indicated by the earlier analyses and suggest that the artist's preferred medium was linseed oil. In some cases, such as the white cloud and the paint of the water in *A Regatta on the Grand Canal*, the oil had been heat-bodied.

When a twentieth-century artist sets out to produce a work purporting to date from an earlier period, the examination of the materials he has used may be particularly interesting. *Portrait Group* (NG 3831) is an early twentieth-century forgery, possibly by the forger Icilio Federico Joni. The profile portraits are supposed to be those of Federigo da Montefeltro, Duke of Urbino (1422–82), and two of his children. The medium of the paint itself is essentially egg tempera, but above this the artist applied a layer of shellac mixed with a little pine resin, probably in the form of a cheap spirit-based varnish. This layer has keyed into the paint beneath. Shellac is rich in reactive hydroxyl groups; free carboxylic acid groups are also available, leading to the possibility of cross-linking to form insoluble esters.[11] As the material cross-linked it would tend to contract, producing a pronounced craquelure in the tempera film below. The presence of drying oil in the infra-red spectrum suggests that the artist oiled out his work before applying an oil varnish containing a triterpenoid resin to complete his 'fifteenth-century' deception.

Paintings of the Dutch School

A survey of the paint media used by Rembrandt and other painters in his circle in paintings in the National Gallery Collection suggested that, on the whole, the most widely used medium was linseed oil, sometimes heat-prepolymerised. Walnut oil was used less often; poppyseed oil was not identified at all.[12] Recently a selection of paintings by the seventeenth-century landscape painters Roelandt Savery, Jan van Goyen, Jacob van Ruisdael and Jan Wijnants was examined, together with two genre scenes by Jan Steen. The earliest picture examined was Savery's *Orpheus* (NG 920), painted in 1628 when he was living in Utrecht; the latest, *A Landscape with Two Dead Trees, and Two Sportsmen with Dogs on a Sandy Road* (NG 972), painted by Wijnants probably around 1665–75. The period covered is thus comparable with that discussed in the earlier study.

Roelandt Savery's picture of Orpheus charming a disparate collection of exotic animals in a mountainous setting is roughly contemporary with Jan van Goyen's *A Cottage on a Heath* (NG 137), of about 1629; stylistically it is a world away. Savery painted in a style derived from the Flemish mannerist 'fantasy' landscape tradition, but drew also on studies made while travelling in the Tyrol. Van Goyen worked in the very much more naturalistic 'tonal' landscape style, of which he was one of the principal architects.[13] His handling is quite free and rapid, with soft rounded touches of unctuous paint particularly apparent in, for example, the white clouds and the cream and brown areas of the foreground landscape. The medium used by both painters is, however, the same: linseed oil. In the case of the cool white cloud and the brown bank in van Goyen's picture the oil used was heat-prepolymerised, giving the soft, rounded impasto of the brushstrokes in these areas. Linseed oil was also identified in the other, rather later, painting by van Goyen examined, *A River Scene, with a Hut on an Island* (NG 6154), painted in the early 1640s.

Chemically speaking, the characteristic feature of heat-bodied oils is that the polymerisation reactions by which the triglyceride molecules present join together have already begun. Whether the linkages are by way of carbon–oxygen or carbon–carbon bonds depends on whether or not oxygen was incorporated into the oil during the heating process: that is, in

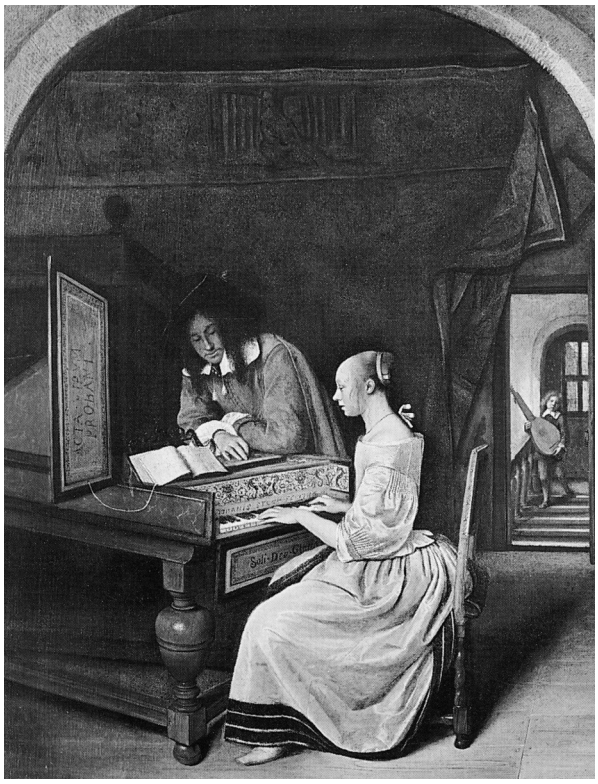

Fig. 3 Jan Steen: *A Young Woman playing a Harpsichord to a Young Man* (NG 856), probably 1659. Oak, 42.3 × 33 cm.

effect, whether it was stirred much during heating and if it was open to the air or covered.[14] For the artist looking for a paint with more body, the net result of prepolymerisation would be the same either way: a rather more viscous product in which the pigments are less likely to sink and which maintains its volume well as it dries, so that there is less likelihood of the film wrinkling. Analysis suggested that the oil used by Savery for the white paint of the rocks in *Orpheus* had been partially heat-bodied, and it is quite possible that he used an oil that had only been subjected to limited heat treatment. Another possible explanation for such a result is that the paint had been prepared using ordinary linseed oil and the artist mixed in a little heat-prepolymerised oil during painting.

For an artist who, like van Goyen, gives the impression of having painted freely and rapidly, the use of a heat-bodied oil in certain passages of his painting to give touches of well-bodied, but smooth, very slightly translucent and plainly easily manipulated paint is entirely appropriate. The same could be said of his son-in-law and former pupil Jan Steen, whose handling of paint was particularly confident and varied. Steen was a notably prolific painter. Eighteenth-century writers commented on the speed with which he worked and recent examination of the condition of certain of his paintings has tended to confirm that he worked extremely quickly. It has also indicated that Steen was indeed a skilful painter with a very clear understanding of the handling properties of his paint.[15] He used a heat pre-polymerised linseed oil in *A Young Woman playing a Harpsichord to a Young Man* (NG 856; Fig. 3), and in *Skittle Players outside an Inn* (NG 2560), painted a little later, around 1660–3.[16] In the former painting it was identified in the brownish paint of the floor, the blue-grey patterned wall-hanging to the left of the door and the young woman's light-blue skirt; in the latter, in the leaves of the trees and the red-brown soil in the foreground. An earlier study of a number of works by the artist also suggested the predominant use of linseed oil, with a limited use of walnut oil; it was not possible at that time to say whether or not the oil had been heat-bodied.[17]

The other Dutch seventeenth-century pictures examined, Jacob van Ruisdael's *A Road winding between Trees towards a Distant Cottage* (NG 988, 1645–50) and Jan Wijnants's *Landscape with Two Dead Trees, and Two Sportsmen with Dogs on a Sandy Road*, were also found to have been painted using linseed oil. The results obtained as a whole bear out the findings of the earlier survey: that the use of linseed oil was by far the most common in mid-seventeenth-century Holland. Walnut oil was used, but less frequently; poppyseed oil, which has occasionally been identified in the works of French painters of this period, has yet to be identified in the work of a seventeenth-century Dutch painter.[18]

The depiction of flowers was a branch of painting for which Dutch artists were particularly noted during both the seventeenth and eighteenth centuries. A recently published account of works by the seventeenth-century painters Jan Brueghel, Balthasar van der Ast and Ambrosius Bosschaert the Younger illustrated the extraordinarily fine technique of the artists and discussed the pigments used; unfortunately no examination of the paint medium was possible.[19] It has, however, been possible to make a limited investigation of the medium used in four eighteenth-century works, by Jan van Huysum and Jan van Os, in the National Gallery Collection. The earliest, Jan van Huysum's *Hollyhocks and Other Flowers in a Vase* (NG 1001), dates from the earlier part of the painter's career, after 1702 but before the early 1720s (Fig. 4).

It might be expected that, with such accurate depiction of the forms and colours of the flowers and the almost palpable texture of the leaves, some attention might have been paid to the quality of the paint media. It is therefore not surprising to find that, while linseed oil was used for the dark brown table and dark green-blue leaves on the right, for example, where any tendency it had to discolour would not be apparent, a heat-bodied walnut oil was used for the white hollyhock in the centre and a pale blue highlight on a blue-green leaf. A similar pattern can be seen in the slightly later *Flowers in a Terracotta Vase* (NG 796) of 1736, where the artist used walnut oil for the white flowers. Walnut oil, which initially yellows less than linseed oil, was traditionally recommended for white, blues and other pale colours. Poppyseed oil is even paler in colour and was used by Jan van Os in *Fruit, Flowers and a Fish* (NG 1380), painted some fifty years later in 1772, for the white rose, whereas linseed oil was used for the mustard-coloured skin on the pomegranate and for the brown background on the left.

Like van Huysum's paintings, van Os's *Fruit and Flowers in a Terracotta Vase* (NG 6520) has an almost tangible realism; close examination of the paint surface reveals that the artist has exploited the illusionistic qualities of impasto for some of the flowers, although how far the paint medium is responsible for these effects must remain an unanswered question in this case. The paint surface is largely in superb condition, but the thick, glossy, dark red glaze on a peony at the lower right has a marked craquelure. It was found to contain linseed oil and a little pine resin; as discussed above, the addition of the resin gives a rich, glossy, transparent glaze, but here – applied thickly – it may also have made the paint rather brittle.

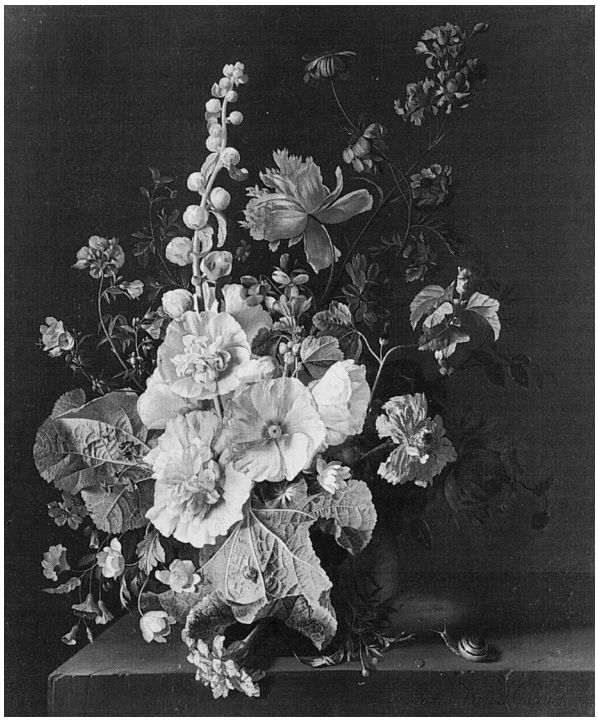

Fig. 4 Jan van Huysum: *Hollyhocks and Other Flowers in a Vase* (NG 1001), 1702–20. Canvas, 62.1 × 52.3 cm.

Nineteenth-century French paintings

It is safe to say that a greater variety and quantity of organic materials were likely to find their way into the paint medium in the latter part of the eighteenth century and in the nineteenth century than in earlier times. The reasons behind this were partly practical: to speed up drying, for example, for the benefit of those who were making rapid sketches, perhaps in the open air; or to add body to the paint; or to alter its appearance or handling properties. There was also an antiquarian element. Much of the continuing interest in wax-containing paint media, for example, derived initially from research into Roman encaustic painting.[20] It was supposed to be durable and less prone to discoloration than oil paint, prompting many investigations into wax-containing paint formulations. Behind the many natural resin varnish mixtures lay much conjecture as to how earlier artists such as Jan van Eyck (who was frequently credited with the invention of oil painting) and the Cinquecento Italian masters could have achieved their effects. (No account was taken of the slight increase in the refractive index of the oil medium that occurs with time, with a resultant increase in translucency, nor, indeed, was this a concept that had yet been formulated.) Speculation was given an added impetus by the discovery of the works of earlier authors, particularly Theophilus, as well as work on earlier varnish recipes. Nineteenth-century French writers on the technology of oil painting, such as J.-F.-L. Mérimée, devoted much attention to the historical aspects of their subject: Mérimée quotes Theophilus's varnish recipes in his section on copal varnishes.[21]

At this time also, fundamental developments were taking place in chemistry in general and organic chemistry in particular: the growing understanding of the nature of chemical elements and the laws governing chemical structure and combination meant that it became possible to predict behaviour. As a result the period was a time of considerable technological progress. The paint industry was not excluded from this: many new pigments were developed, for example.[22]

There was also a growth in the understanding of the chemistry of both pigments and medium. In the late 1840s, Michel Eugène Chevreul carried out a series of experiments on the drying of oils and the influences of particular pigments, supports, diluents, driers and methods of processing on linseed oil. He demonstrated the importance of oxygen in the drying process and the effects of heating the oil with or without drying salts, basing his investigations (which he carried out with the help of E.-C. Leclaire, better known for his work on zinc white and other zinc-containing pigments) on the production methods generally in use.[23] His research was of fundamental importance and was still being cited many years later.

Two new factors came to influence the manufacturers of artists' materials: the growth in popularity of landscape painting out of doors and the rise of the amateur market. Colour merchants' catalogues show that, as the nineteenth century progressed, the number of products developed for the convenience of the painter – proprietary media for different purposes; easily portable easels and paint boxes; light, inexpensive supports of millboard and paper mounted onto backings as well as the conventional panels and canvases – greatly increased. Manuals to help the amateur painter were published in ever-increasing numbers and from these it is possible to learn how the products might be used. The examination of a number of works by mid-nineteenth-century landscape painters, including Camille Corot and several others associated together under the name of the Barbizon School, Charles-François Daubigny, Théodore Rousseau, Narcisse Diaz de la Peña and Jules Dupré, as well as contemporaries like Gustave Courbet, has been able to show something of how these various strands of influence came together in the products the artists used.

It is important to remember that, in spite of the undoubted enthusiasm of the painters for their open-air studies, the painting produced was often completed in the studio and might, indeed, be a study for a larger and more conventionally finished product.[24] The materials used would have been largely the same whether painting was done in the open or in comfort indoors, but examination of the paint layer structure in many of these paintings has provided clear evidence that work took place over more than one painting session and that modifications were made, no doubt often in the studio.[25] In this study, there have been few cases where it has been possible to examine the constituents of the paint medium layer by layer; where this has been done it has not usually shown sufficiently marked differences between the layers to confirm this. In one case, Corot's *Landscape at Arleux-du-Nord* (NG 6531), which was apparently begun during a trip to Arleux in 1871 and completed in the artist's Paris studio in 1874, examination of the paint medium in an area of dull green water which appeared to be part of the earlier campaign showed that the artist used a medium of linseed oil containing some pine resin. A touch of brighter green added during his later work on the painting in the studio, however, contained heat-bodied walnut oil and a trace of copaiba or a similar resin.[26]

The paintings studied range in date from Corot's *The Roman Campagna, with the Claudian Aqueduct* (NG 3285) probably painted in 1826, to paintings by Daubigny, Diaz and indeed Corot himself, painted in the 1870s. Some developments in paint technology might be expected over a period of some half a century. These are perhaps more easily demonstrable in the pigments used than in the paint medium, particularly when the sample of paintings examined is relatively small. The presence of dammar resin, in what is probably an oil varnish product used as an additive (like copal varnish), in two paintings by Daubigny, *Willows* (NG 2621), probably painted in 1874, and *Landscape with Cattle by a Stream* (NG 6324), of 1872, is interesting in this respect. Dammar seems to have been used for the first time on its own merits as a picture varnish in 1829, becoming more widely used for this purpose only later. It was sometimes suggested as a substitute for copal in varnishes, however, which may explain the occurrences in Daubigny's paintings. It seems also that, because of the general confusion in the identification of similar-appearing materials, purchasers of the resins were not always able to distinguish clearly between them: in other words it may have been mistaken for copal, or used as a copal-like material.[27]

Documentary sources throughout the century suggest that, while poppy oil might be the best in which to grind the pigments, as it was the palest, walnut or linseed oils might be used in practice; linseed was the most drying and was recommended for poorly drying pigments, but it was the darkest; walnut oil was paler and the lesser drying.[28] The results obtained from paintings by Corot, and some of those by Diaz, Daubigny and Rousseau, show that the pigments were frequently ground in walnut oil. The only painting from the group to have pigments ground in the supposedly superior, paler, poppyseed oil is Jules Dupré's *Willows, with a Man Fishing* (NG 2634), probably painted before 1867; it was identified in the

blue sky and, heat-bodied, in the dark green foreground paint.

One of the most significant developments for those who painted out of doors and for amateurs was that of the collapsible metal tube in 1841.[29] In the 1820s and 30s, when some of the earlier paintings examined, such as Corot's *Roman Campagna* and *The Seine near Rouen* (NG 4181, 1830–5) and Rousseau's *Sunset in the Auvergne* (NG 2635) and *The Valley of St-Vincent* (NG 3296), of about 1830, and *A Rocky Landscape* (NG 4170), of about 1836–40, were painted, paint was sold in bladders. Bladders were still available during the 1850s, co-existing with the paint tube; by the 1870s the tube had taken over. In both cases, the colour merchant would have to overcome the problem of shelf life: paint settling or drying in the container was undesirable. It is interesting to note that, in some cases, such as the poppyseed oil Dupré used in the sky of his painting and the walnut oil identified in the sky of Corot's *The Leaning Tree Trunk* (NG 2625) of about 1855–60, the oil is unmodified. In many others, however, such as the white paint in the sky of the same picture by Corot, the oil has been heat-bodied and, it seems, was purchased as such. In the discussion of the paintings of the Dutch School above (pp. 77–9), it has already been stated that heat-prepolymerisation produces a more viscous product, in which the pigment would be less likely to settle out; from this point of view the use of a heat-bodied oil is highly appropriate. From the discussion above of the North Italian School painting of *Saint Hugh* (p. 74), however, it might be thought also that the oil would dry more rapidly: hardly suitable for paint storage and an extended shelf life. In practice, there is a reason why this is not the case.

The method of producing a heat-prepolymerised oil has an influence on the rate of drying, depending on the bonds produced and whether or not the oil was heated over a drier. Although oils approaching the modern stand oil, heated to about 300–320°C in a closed container from which oxygen is excluded, were produced during the latter part of the nineteenth century, this is not the type of heat-bodied oil present in the majority of nineteenth-century (or earlier) paintings. For these, the method of production was based on the traditional one used over preceding centuries: the oil was heated gently to a temperature at which bubbles of steam (from absorbed moisture) and carbon dioxide are produced (about 230°C) for several hours, for the latter part of the time over lead or manganese salts. Chevreul showed that this oil, if produced without driers, dried a little more rapidly than a raw, untreated oil; in practice the oil was commonly heated with metallic salts and dried considerably more rapidly, even if the heating temperature was only 70 or 80°C.[30] A good proportion of the bonds produced in such a product will be carbon–oxygen (in a modern stand oil, the bonds produced are principally carbon–carbon) as it is generally stirred and air is not usually excluded. In a paint film, this product, which is comparable with a modern 'boiled' oil, congeals and consolidates more rapidly than an untreated oil, explaining its use with poorly drying pigments. In the massive state, however, as found in a tube of paint, this may not be the case: as air and the catalytic effect of light are excluded, further polymerisation by the formation of carbon–oxygen linkages cannot proceed and the shelf life of the product may, in fact, be extended. Also it is impossible to know whether or not the heat-bodied oil apparently present in tube paint had been processed over driers.

For both painting out of doors and the growing amateur market there was an obvious need for quick-drying products so that effects could be captured or the sketch jotted down and taken back to the studio if desired for completion. The heat-bodied oil described above was such a product and was commonly known as *huile grasse*; it was usually prepared from linseed oil. Jean-Pierre Thenot, in a discussion of the materials necessary for landscape studies out of doors published in a manual of 1842, wrote that little bottles of *huile grasse* and poppyseed oil should be taken, as well as a little phial of *vernis copal*.[31] Daubigny, on a painting trip in Le Bourg-d'Oysans in 1839, wrote to his brother-in-law back in Paris asking for a supply of pigments and '*des bonnes huiles grasses*' as he had none left.[32] Some of the findings of heat-prepolymerised oils listed in the Table can surely be attributed, at least in part, to the use of products such as this.

In order to ensure that paint dried more rapidly, the artist could modify the medium in other ways. The addition of diluent, in the form of spirits of turpentine, would give the impression of more rapid drying because evaporation of the turpentine would leave a lean, matt paint that would quickly appear to be touch-dry; in fact, as Chevreul demonstrated, properly speaking, turpentine had no genuine siccative effect.[33] The diluted, fluid paint produced was eminently suitable for use at an early stage in the production of the picture, when the principal elements of the composition were freely and roughly blocked in. The artist could also add a siccative to his paint on the palette;

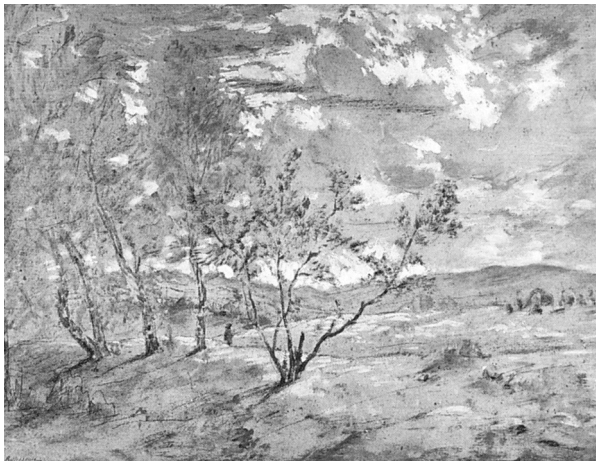

Fig. 5 Pierre-Etienne-Théodore Rousseau: *Landscape* (NG 5781), probably 1860–5. Millboard, 49.8 × 67 cm.

this might be something like lead acetate (*sel de Saturne*), which could be used in crystalline or paste form, or a proprietary drier. The two most frequently referred to during this period are the so-called *Siccatif de Courtrai* and *Siccatif de Haarlem* [or *Harlem*]. There appear to have been no patents for either of these products and the formulation for the former seems to have been slightly variable; however, it is clear that *Siccatif de Courtrai* was based on linseed oil, heated with a very high proportion of lead or manganese oxides (or both), perhaps with the addition of turpentine spirit. It is described as being very dark in colour, which was one of its disadvantages, but it would indeed have encouraged the oil film to dry by the absorption of oxygen and by cross-linking.[34] In 1865 Jean-François Millet wrote from Barbizon to his colour merchant in Paris asking for four *flacons* of the drier and although there were many who complained of its ill effects it was undoubtedly widely used.[35] It could be kept in a *godet* attached to the palette and the brush dipped in whenever needed, so it was all too easy to use too much. A large proportion could also be added to the paint to give a very runny, but quick-drying, paint for the *ébauche* (preliminary painting or lay-in).[36] It is not easy to detect its presence analytically, however.

Siccatif de Haarlem was invented by a Paris pharmacist, A.M. Duroziez, perhaps around 1840.[37] It became extremely popular and its inventor was awarded an honourable mention at the Paris trade fairs of 1844 and 1849. It appears to have been essentially a copal varnish, perhaps with much diluent. Like the *Siccatif de Courtrai*, it could be used in a thin, quick-drying paint for the preliminary stages of painting, and it is possible that this drier is the source of the copal detected in Théodore Rousseau's *Landscape* (NG 5781), probably painted in 1860–5 (Fig. 5), rather than a copal varnish as such. The painting is thought to represent an early stage in the work, perhaps sketched in the open air; the paint is lean in medium and traces of copal were detected in samples of blue and white paint from the sky, together with heat-bodied walnut oil. This rather suggests the use of a quick-drying paint in which a volatile diluent was originally present. The trace of copal detected in the green paint of the trees on the right of Corot's *Evening on the Lake* (NG 2627), of about 1872, may be due to the use of a similar drier; the other constituents of the paint medium were heat-bodied walnut oil and mastic resin.

Rousseau had a reputation for being somewhat careless in his over-enthusiastic use of painting media of uncertain reputation and of the poorly drying brown pigment mummy. After his death, Jules Dupré wrote to his biographer Alfred Sensier that the fact that one of Rousseau's finest paintings of the mid-1830s had failed to survive intact was due to his injudicious use of a medium consisting of two-thirds *huile grasse* and one-third of a proprietary varnish, a *vernis double* (perhaps a mastic/turpentine varnish), together with bitumen mixed with wax. Sensier indeed confirms Rousseau's use of mummy during the 1850s.[38] In a transparent brown glaze in an area of the foreground in Rousseau's *Landscape*, there appeared to be a trace of mastic as well as the heat-bodied walnut oil and copal detected in the other samples. However, the mastic component detected, 28-norolean-17-en-3-one, is a pyrolitic decomposition product only produced on intense heating. Heated conifer resin products and a trace of beeswax were also present. The overall pattern is one that has only previously been detected in samples of mummy and it seems that mummy is indeed the brown pigment Rousseau used for his glaze.[39]

A large proportion of the paintings examined reveal the presence of natural resins in the paint, often pine, sometimes mastic or copal or fir, or, indeed, a mixture. If the copal does not derive from the use of *Siccatif de Haarlem*, contemporary colour merchants' catalogues reveal that it could be present in the form of *huile copal* or *vernis copal*; both seem to be essentially drying oil and copal, although literary sources suggest that linseed oil was generally used for preparing copal varnishes, while walnut oil was more frequently detected in the paint samples.[40] Given

the number of ways in which copal could be introduced into the paint, it is usually difficult to say precisely which product is involved. The addition of a varnish to the paint would have added gloss, but it was also frequently recommended to prevent the colours sinking and they dried quickly. They also had particular, and versatile, handling properties: Mérimée described the properties of copal varnish as rendering the colours more brilliant and the paint more unctuous, but not drying too rapidly; the gel-like *vernis des Anglais* (essentially megilp, mastic varnish shaken with drying oil) was good for glazes because it spread very easily, but maintained its shape on the palette without flowing about.[41] Examination of Corot's *The Roman Campagna, with the Claudian Aqueduct* revealed the presence of a trace of pine resin and a trace of mastic in the green paint of a hedge; this may represent a use of the notorious *vernis double* which Dupré accused Rousseau of using, although here it seems perfectly stable.[42]

Copal in the form of varnish or *huile copal* is present with linseed oil in white paint in *Seascape with Figures on Cliffs* (NG 6416), painted by a follower of Corot around 1865–75; with heat-bodied walnut oil it occurs in white paint on a rock in the foreground in Diaz's *Sunny Days in the Forest* (NG 2058), probably painted around 1850–60, and in green paint (mixed with fir balsam) in *The Storm* (NG 2632) of 1871. Interestingly, the presence of a high proportion of isoagathic acid in this sample, formed as the result of the strong heating necessary to get the copal into a soluble form, suggests that the varnish had been well heated and may have been quite dark in colour, rather as one might expect for a coach varnish or something similar. The presence of the fir balsam in this paint may be connected with this. Pine resin mixed with copal occurs in very hard, glossy green paint in Daubigny's *Alders* (NG 2623) of 1872 and is not uncommon in varnish recipes of this period. Adulteration of the copal at the point of purchase may be one cause, but it is just as likely to have been added deliberately; it produces a perfectly satisfactory varnish at less cost and with considerably less trouble than copal.

Notes and references

1. R. White and J. Kirby, 'Rembrandt and his Circle: Seventeenth-Century Dutch Paint Media Re-examined', *National Gallery Technical Bulletin*, 15, 1994, pp. 64–78, esp. pp. 71–3, 78; R. White and J. Pilc, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 17, 1996, pp. 91–103, esp. pp. 94, 98–9; 'Methods and materials of Northern European painting in the National Gallery 1400–1550', *National Gallery Technical Bulletin*, 18, 1997, pp. 6–55, esp. pp. 42, 53–4.
2. G.B. Armenini, *De' veri precetti della pittura*, Ravenna 1587; addition of varnish to glazes, pp. 126–8; addition of varnish to black, p. 124: '… perche questa vernice è di tal qualità che dà forza, e aiuto à tutti i colori, che patiscono nell' asciugarsi'. Seventeenth-century authors among others sometimes suggested (with no great foundation in fact) that the addition of varnish would improve drying; this would be an understandable reason for making such an addition to both red and black glazes and cannot be excluded, but it is probably not what Armenini means here. Armenini was a great believer in adding varnish to the paint, including the *imprimitura*, something he could have noted in the writings of Leonardo da Vinci, which he probably saw during a trip to Milan during the late 1550s or early 1560s. There is as yet little evidence that the incorporation of varnish in preparatory paint layers was at all common in easel painting of the period. In the case of the glazes, however, it seems he is describing current practice to some extent.
3. White and Kirby 1994, cited in note 1, pp. 68–71.
4. J. Pilc and R. White, 'The Application of FTIR–Microscopy to the Analysis of Paint Binders in Easel Paintings', *National Gallery Technical Bulletin*, 16, 1995, pp. 73–84, esp. p. 82.
5. The pigments and paint layer structure in these three paintings were examined and identified by Ashok Roy using optical microscopy and SEM–EDX.
6. M. Zerdoun Bat-Yehouda, *Les encres noires au Moyen Age*, Paris 1983; see for example pp. 289–98; P. Arpino, J.P. Moreau, C. Oruezabal and E. Flieder, 'Gas chromatographic–mass spectrometric analysis of tannin hydrolysates from the ink of ancient manuscripts (XIth to XVth century)', *Journal of Chromatography*, 134, 1977, pp. 433–9.
7. A. Braham and J. Dunkerton, 'Fragments of a Ceiling Decoration by Dosso Dossi', *National Gallery Technical Bulletin*, 5, 1981, pp. 27–37, esp. pp. 30–3.
8. J. Dunkerton, J. Kirby and R. White, 'Varnish and Early Italian Tempera Painting', *Cleaning, Retouching and Coatings: Preprints of the Contributions to the IIC Brussels Congress, 3–7 September 1990*, edited by J.S. Mills and P. Smith, London 1990, pp. 63–9, esp. pp. 66–7.
9. Examination of the pigments and paint layer by Marika Spring, using optical microscopy and SEM–EDX.
10. D. Bomford and A. Roy, 'Canaletto's "Venice: The Feastday of S. Roch"', *National Gallery Technical Bulletin*, 6, 1982, pp. 40–3, esp. p. 42, and J. Mills and

R. White, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 7, 1983, pp. 65–7; R. White and J. Pilc, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 14, 1993, pp. 86–94, esp. p. 88.

11. J.S. Mills and R. White, *The Organic Chemistry of Museum Objects*, 2nd edn., London 1994, pp. 115–18.
12. White and Kirby 1994, cited in note 1, pp. 64–78, esp. p. 67.
13. N. MacLaren, *The Dutch School 1600–1900, National Gallery Catalogues*, revised by C. Brown, 2 vols., London 1991, Vol. 1 (text), pp. 143, 148, 411–3; E.M. Gifford, 'Style and Technique in Dutch Landscape Painting in the 1620s', *Historical Painting Techniques, Materials and Studio Practice: Preprints of a Symposium, University of Leiden, the Netherlands, 26–29 June 1995*, edited by A. Wallert, E. Hermens and M. Peek, Marina del Rey 1995, pp. 140–7. For a discussion of Dutch landscape painting of this period see C. Brown, *Dutch Landscape, the Early Years: Haarlem and Amsterdam 1590–1650*, exh. cat., National Gallery, London 1986.
14. White and Kirby 1994, cited in note 1, pp. 68–71; Mills and White 1994, cited in note 11, pp. 36–41.
15. M. Bijl, 'The Artist's Working Method', in H.P. Chapman, W.Th. Kloek and A.K. Wheelock, *Jan Steen: Painter and Story Teller*, exh. cat., National Gallery of Art, Washington, Rijksmuseum, Amsterdam, 1996/7, pp. 83–91, esp. pp. 85, 89–90.
16. MacLaren/Brown 1991, cited in note 13, p. 423.
17. M.H. Butler, 'Appendix: An Investigation of the Technique and Materials Used by Jan Steen', *Jan Steen: Comedy and Admonition*, special issue of the *Bulletin of the Philadelphia Museum of Art*, 78, nos. 337–38, Winter 1982 – Spring 1983, pp. 44–61, esp. p. 46. The statement that walnut oil was identified in a sample from a green leaf in *The Fortune Teller* (Philadelphia Museum of Art, W.P. Wilstach Collection) is an error; the quoted palmitate/stearate ratio of 1.7 is well within the range for linseed oil. Walnut oil was thought to be present in some creamy white paint at the top edge of this painting; the palmitate/stearate ratio obtained, 2.3, is just within the walnut oil range. The analyses were carried out by John S. Mills in the National Gallery Scientific Department.
18. White and Pilc 1996, cited in note 1, pp. 91–103, esp. p. 93.
19. S. Murray and K. Groen, 'Four early Dutch flower paintings examined with reference to Crispijn van de Passe's "*Den Blom-Hof*"', *Hamilton Kerr Institute Bulletin*, 2, 1994, pp. 6–20.
20. See, for example, A.-C.-P. Caylus, Comte de, *Mémoire sur la peinture à l'encaustique et sur la peinture à la cire*, Geneva 1755; D. Rice, *The Fire of the Ancients: the Encaustic Painting Revival 1755 to 1812*, PhD dissertation, Yale University 1979, Ann Arbor 1979 (rep. 1989).
21. See, for example, F. Bonanni, *Trattato sopra la vernice detta comunemente cinese*, Rome 1720, French trans. Paris 1723 and several later edns.; G.E. Lessing, *Vom alter der Oelmahlerey, aus dem Theophilus Presbyter*, Braunschweig 1774; a French translation of part of this may be found in C.F. Soehnée, *Recherches nouvelles sur les procédés de peinture des anciens*, Paris 1822; J.-F.-L. Mérimée, *De la peinture à l'huile*, Paris 1830 (facsimile edn. Puteaux 1981). It is clear from the introduction to the book, by the Secretary of the Académie des Beaux-Arts, A.-C. Quatremère de Quincy, that the origins of oil painting were of great interest; in Mérimée's text there is much discussion of the van Eycks, and the paintings of earlier artists like Titian, Correggio, Fra Bartolommeo, Rubens and Rembrandt also form a constant theme. For Theophilus's varnish recipes see pp. 71–4.
22. For a simple account of the chemistry of this period see J. Hudson, *The History of Chemistry*, London 1992; for a discussion in depth see J.R. Partington, *A History of Chemistry*, Vol. III, London 1962 (1970 reprint). For a brief account of the effects on paint technology (particularly pigments) see D. Bomford, J. Kirby, J. Leighton and A. Roy, *Art in the Making: Impressionism*, exh. cat., London 1990/1, pp. 51–67.
23. M.-E. Chevreul, 'Recherches expérimentales sur la peinture à l'huile', *Annales de Chimie et de Physique*, 3^{e} série, XLVII, 1856, pp. 209–83.
24. J. Leighton, '"Bienheureux les paysagistes!" Landschaftmahlerei unter freiem Himmel', *Corot, Courbet und die Mahler von Barbizon*, eds. C. Heilmann, M. Clarke and J. Sillevis, exh. cat., Munich 1996, pp. 23–31.
25. A. Roy, 'Barbizon Painters: Tradition and Innovation in Artists' Materials', *Barbizon. Malerei der Natur und Natur der Malerei*, papers given at the International Symposium held in Munich, 7–9 March 1996, in course of publication. The results of medium analysis quoted in this paper were those of a preliminary stage of the investigation.
26. A. Robaut, *L'Œuvre de Corot*, 4 vols, Paris 1905, Vol. III, p. 252, no. 2017.
27. N.-J.-B.-G. Guibourt, *Histoire abrégée des drogues simples*, 3rd edn., 2 vols, Paris 1836, pp. 525–9 (copal) and 535–7 (dammar). Guibourt wrote a greatly extended account of these resins in the *Revue scientifique et industrielle*, February 1844, part of which was printed in A.-M. Tripier-Deveaux, *Traité théorique et pratique sur l'art de faire les vernis*, Paris 1845, pp. 73–99. Guibourt noted that so-called *dammar tendre* was often sold under the name of *copal tendre*: see pp. 78, 93. See also A. Livache, *Vernis et huiles siccatives*, Paris 1896, pp. 123–7.
28. J. Panier, *Peinture et fabrication des couleurs*, Paris 1856, pp. 17–18; R. Lemoine and Ch. du Manoir, *Les matières premières employées en imprimerie, arts & peinture*, Rouen 1893, pp. 13–36.

29. R.D. Harley, 'Oil Colour Containers: Development Work by Artists and Colourmen in the Nineteenth Century', *Annals of Science*, 27, 1971, pp. 1–12.
30. Chevreul 1856, cited in note 23, pp. 252–62.
31. J.-P Thénot, *Essai de peinture à l'huile: Manuel indispensable à toute personne qui s'occupe de ce mode de peinture*, Paris 1842, p. 8.
32. M. Fidell-Beaufort and J. Bailly-Herzberg, *Daubigny*, Paris 1975, letter V, p. 241.
33. Chevreul 1856, cited in note 23, pp. 237–43.
34. Chevreul, for example, showed that the addition of drying linseed oil, prepared wih a manganese oxide drier, to four times its volume of ordinary raw linseed oil caused the oil to dry very satisfactorily; see Chevreul 1856, cited in note 23, pp. 210–15. For comments on the colour and other properties of these driers see J.-G. Vibert, *La Science de la peinture*, 4th edn., Paris 1891, pp. 127–31; E. Dinet, *Les Fléaux de la peinture: Observations sur les vernis, les retouches et les couleurs*, Paris 1904, pp. 54–5.
35. J. Sillevis and H. Kraan, *L'Ecole de Barbizon: un dialogue Franco-Néerlandais*, exh. cat., Museum voor Schone Kunsten, Ghent 1985; letter to the colour merchant Blanchet, 8 February 1865, p. 210.
36. K. Robert [i.e. G. Meusnier], *Traité pratique de la peinture à l'huile*, Paris 1878, pp. 16–18.
37. Duroziez refers to it in passing, without divulging its ingredients, in the second edition of his small manual, *Manuel du peintre à la cire*, Paris 1844, but it is not mentioned in the earlier edition of *c.*1838. See also the later edition entitled *Considérations sur la peinture à l'huile*, Paris 1849.
38. A. Sensier, *Souvenirs sur Th. Rousseau*, Paris 1872, pp. 77–8, 201. The medium described would be similar to an English megilp. The painting concerned was the *Descente des vaches des hauts plateaux du Jura*, submitted to the Salon of 1836, but refused.
39. M. Serpico and R. White in A. Lucas, *Ancient Egyptian Materials and Technology*, rev. edn., forthcoming Cambridge 1998.
40. *Copal à l'huile* is listed among the products sold by Duroziez: see Duroziez 1844, cited in note 37, pp. 309–10. The catalogue produced by the colour merchants Lefranc et Cie in 1876, for example, listed both *huile copal* and *vernis copal* (p. 6). For the preparation of these materials see Livache 1896, cited in note 27, pp. 64, 80–5, 115–23; A. Romain, *Nouveau manuel complet du fabricant de vernis de toute espèce*, Paris 1888, pp. 184–92, 262–7.
41. Mérimée 1830 (1981 reprint), cited in note 21, pp. 65–91.
42. A. Ducrot, *La peinture à l'huile et au pastel apprises sans maître*, Paris 1858, p. 23.
43. The palmitic/stearic ester ratio (P/S) was of a value (2.0) intermediate between linseed and walnut oils, and may not truly represent an accurate assay on account of being an extremely small sample, for which the background lipids may not be neglected.
44. A P/S ratio of 2.4 was obtained.
45. A little bluish re-touching seems to have been gathered in this sample. This was crudely separated out and GC–MS suggested the use of linseed oil. The residue, essentially original paint, was identified as having a heat-bodied walnut oil binder by GC–MS.
46. No 'copper resinate' detected by FTIR–microscopy.
47. Negligible lipids present in the ink layer by FTIR–microscopy, although this technique did indicate some lipids associated with the blue sky paint above, characterised as walnut oil by GC–MS. Direct Insertion Heated probe investigation of a fragment of the ink on the mass spectrometer produced poor results and gave no clear indication of the volatilisation of compounds likely to be derived from an iron-gall ink. A further fragment was retained for other pyrolysis/thermolysis investigations. No resin was detected, either by FTIR–microscopy or GC–MS. For further discussion see text pp. 75–6.
48. This paint had the appearance of being very thick and 'bodied'. There was no evidence for 'copper resinate', but FTIR–microscopy suggested a resin-content that was strongest towards the top of the layer, where it became of a more brownish-green appearance under the microscope – though, seemingly, not a distinct 'varnish' layer as such.
49. This paint had a complex layer structure and consisted of a reddish-brown layer with a varnish layer (fluorescing in ultraviolet light) above, surmounted by blue paint. Although the paint appeared to contain a drying oil medium (by FTIR–microscopy), the intermediate varnish layer was identified as sandarac resin. Subsequent GC–MS analysis of fragments of the separated layers showed the medium of the paint below and above the fluorescing layer to be heat-bodied walnut oil. The fluorescing varnish layer contained a sandarac-like terpenoid resin.
50. See text, p. 77.
51. Analysis by FTIR–microscopy; too small for GC–MS analysis.
52. The lower main paint layer appears to be egg tempera, with a toning of shellac mixed with pine resin which has been 'keyed' into the paint. This seems to have been 'oiled out' and a final triterpenoid resin/oil varnish has been applied over the whole. For further discussion see text, p. 77.
53. The linseed oil appeared to have been partially heat-bodied with a dimethyl azelate/suberate ratio of 5.3.
54. Further samples examined by GC–MS to check for resin, which might have been missed in the GC study reported in J. Mills and R. White, 'Analysis of Paint Media', *National Gallery Technical Bulletin,* 3, 1979, p. 67.
55. The picture was given to the National Gallery by Sir George Beaumont, 1823/8. A worn inscription on the painting states that it was bequeathed to Beaumont by

Sir Joshua Reynolds in 1792 and it is tempting to surmise that he carried out the repainting in the sky. The medium present is a quite complicated mixture (particularly by comparison with the original paint) and, as Reynolds was known for his interest in the formulation of paint media with various resinous components, it would be no surprise if he was responsible for this one.

56. These samples were examined by gas chromatography only. As a result, the presence of natural resins may have been missed. Previous findings were reported in the *National Gallery Technical Bulletin*, 5, 1981, p. 67.
57. Traces of agathic acid were identified by mass spectrometry, suggesting the addition of copal to the paint, but only in trace amounts. This may represent the addition of a drier of the *Siccatif de Haarlem* type to the medium. See text for a discussion of minor resinous additives, pp. 81–3. It is worth noting that, unless stated to the contrary, no sandaracopimaric acid was detected, suggesting that the copal is not from a tree of the Araucariaceae type: that is, not Manila copal, a kauri or another resin from *Agathis* spp. In fact the agathic acid is probably the enantiomeric form (enantioagathic acid), which, being an optical isomer, has identical chemical and chromatographic properties. This suggests that the copal used was one of the hard African or South American copals, from a tree of the Leguminosae type.
58. A P/S of 2.8, would normally indicate walnut oil, but the somewhat reduced level of dimethyl azelate and pronounced presence of methyl tetracosanoate must represent a moderate presence of beeswax, probably from conservation treatment.
59. The small, but significant, amounts of agathic acid identified by GC–MS suggest the addition of copal to the paint in the form of a trace of painting varnish or *huile copal*, rather than as a drier. See text pp. 82–3.
60. This paint was relatively plastic, compared with the other paints sampled. It appears to run around the margins of the panel only. The walnut oil is certainly heat-bodied, but there are no detectable additives which might account for the comparative softness of the paint. Nor, indeed, does the paint appear to be particularly high in medium content, relative to pigment. It is possible that this is a stand oil, from which oxygen was rigorously excluded during the 'bodying' process and no driers were used during its preparation. See discussion in text, p. 81.
61. This sample was taken from an area of thicker paint (compared with that of sample 6) where some shrinkage had occurred. This may be the result of the presence of camphor within the body of the paint, presumably added as a plasticising component. Its high vapour pressure and the thickness of the paint has caused uneven loss of the camphor, resulting in contraction of the paint surface, while deep down the medium is still relatively soft and plastic.
62. Very minor traces of agathic acid indicated the presence of a hard copal in the paint, but in such small quantity that it could be as a result of the addition of a drier, rather than a painting varnish or *huile copal*; see text, p. 82.
63. The agathic acid content of this sample appeared to be almost entirely isoagathic acid, presumably formed during prolonged strong heating.
64. An unusually complex and curious mixture of materials appeared to be present in the glaze. GC–MS established the presence of moronic acid in the sample, as well as significant amounts of 28-nor-olean-17-en-3-one, a decarboxylation product formed by the tarring of resin from trees of the genus *Pistacia*. The use of a pitch or tar derived from gum mastic (i.e. *Pistacia lentiscus* resin) seems bizarre and, frankly, unlikely. In addition there is evidence for the admixture of a heated conifer resin (retene and 7-oxodehydroabietic acid indicators detected) and traces of higher fatty acids derived from esters of beeswax. Such an unusual combination of materials has been found – ready made – during investigations of authentic samples of ancient Egyptian mummy and funerary preparations, carried out for comparison with organic glazing pigments, such as powdered mummy. For a discussion of the nature of powdered mummy see R. White, 'Brown and Black Organic Glazes, Pigments and Paints', *National Gallery Technical Bulletin*, 10, 1986, pp. 59–62 and references therein. Pistacia resin, particularly the heated form – sometimes alone, sometimes mixed with heated conifer resin, and sometimes including beeswax or fats – seems a relatively common component. The source would not have been *Pistacia lentiscus* but, rather, the more copious resin-producing tree, *Pistacia atlantica* Desf. See J. S. Mills and R. White, 'The Identity of the Resins from the Late Bronze Age Shipwreck at Ulu Burun (Kaş)', *Archaeometry*, 31, 1, 1989, pp. 37–44.
65. Apart from the glaze, these samples appeared rather lean in medium for their size. It is likely that the copal present derives from the use of a proprietary drier; see text p. 82.

Table of Results

ITALIAN SCHOOLS

Artist	Picture	Date	Sample	Medium	Note
Paolo Uccello	*Saint George and the Dragon* NG 6294 Canvas	*c.*1460	1. Blue-green sky with complex layer structure:		
			a. Mainly blue-green paint	Walnut oil, no resin	
			b. Orange underpaint	Heat-bodied drying oil, probably walnut oil[43]	
			c. A fragment of white underpaint, beneath both samples a and b	Walnut oil[44]	
			2. Lime-green grass	Walnut oil[45]	
			3. Greyish-pink path; original orangish-pink paint	Heat-bodied walnut oil	
Piero di Cosimo	*A Satyr mourning over a Nymph* NG 698 Poplar panel	*c.*1495	1. Opaque green of foliage, lower right-hand edge	Heat-bodied walnut oil + some pine resin[46]	
			2. Dark blue sky, top edge, right-hand side	Walnut oil	
			3. Underdrawing from an area where sky is reticulated	Traces of polysaccharide from a gum component (?) of the ink	Underdrawing has affected the paint above[47]
			4. Thickly painted 'muddy' green leaf, top left	Walnut oil + a little pine resin[48]	
	The Fight between the Lapiths and the Centaurs NG 4890 Wood panel	probably 1500–15	1. Dark brown foliage at edge of trees, right-hand side	Walnut oil + a little pine resin	
			2. Pale blue sky	Walnut oil	
	Forest Fire (Ashmolean Museum, Oxford) Poplar panel	*c.*1505	1. Green leaf of trees in background, top edge	Heat-bodied walnut oil + a little pine resin	
			2. Blue sky, top edge above bird's wing	Heat-bodied walnut oil	
Francesco Bissolo	*The Virgin and Child with Saint Paul and a Female Martyr* NG 3915 Wood panel	probably 1505–30	1. Cool white of Virgin's headdress	Linseed oil	
			2. Red glaze-paint, Virgin's left leg	Linseed oil + pine resin	
			3. Darker green glaze paint of female martyr's cloak, right-hand edge	Linseed oil + pine resin	
Dosso Dossi	*A Man embracing a Woman* NG 1234 Poplar panel	probably *c.*1524	1. Greenish-blue background, upper edge		
			a. Brownish layer below intermediate varnish layer	Walnut oil, heat-bodied	
			b. Intermediate layer, fluoresces under ultra-violet illumination	Sandarac varnish	
			c. Blue paint above layer b	Walnut oil, heat-bodied[49]	

ITALIAN SCHOOLS (continued)

Artist	Picture	Date	Sample	Medium	Note
Italian, North	*Saint Hugh* NG 692 Wood panel	*c.*1525–1600	1. White paint of figure's left shoulder	Walnut oil	
			2. Black paint of background	Heat-bodied walnut oil + pine resin	
Attributed to **Sebastiano** del Piombo	*Portrait of a Lady with the Attributes of Saint Agatha* NG 24 Canvas	*c.*1540	1. Brownish background, beneath the symbols of martyrdom; a tinted, intermediate varnish layer	Linseed oil with a conifer resin	Traces of the terpenoid larixol identified the resin as Venice turpentine from a tree of the genus *Larix*[50]
Canaletto	*Venice: The Basin of San Marco on Ascension Day* NG 4453 Canvas	*c.*1740	1. White impasto paint of cloud	Partially heat-bodied linseed oil	
			2. Black paint of gondola	Linseed oil	
			3. Blue highlight of wave	Drying oil medium[51]	
	A Regatta on the Grand Canal NG 4454 Canvas	*c.*1740	1. White cloud	Heat-bodied linseed oil	
			2. Blue-green water of canal	Heat-bodied linseed oil	
	Eton College NG 942 Canvas	*c.*1754	1. Pale blue sky	Linseed oil	Rather lean in medium
			2. Light green leaf of tree, left-hand side	Linseed oil	
			3. Brownish green of shaded bank in foreground	Linseed oil	
Italian	*Portrait Group* NG 3831 Wood panel	early 20th century	1. White robe	Essentially egg tempera	A double layer of varnish also present: *a.* shellac + pine resin 'keyed' into the paint; *b.* drying oil; triterpenoid resin/oil varnish[52]
			2. Red-brown paint of arch	Essentially egg tempera, much the same as sample 1	
			3. Grey-blue sky, left-hand side	Essentially egg tempera, much the same as sample 1	

DUTCH SCHOOL

Artist	Picture	Date	Sample	Medium	Note
Roelandt **Savery**	*Orpheus* NG 920 Oak panel	1628	1. Cool white paint of rocks	Linseed oil[53]	
			2. Dark brown of foliage	Linseed oil	
Jan van **Goyen**	*A Cottage on a Heath* NG 137 Oak panel	*c.*1629	1. Cool white of cloud, top edge	Heat-bodied linseed oil	
			2. Dark brown earth, right-hand edge	Heat-bodied linseed oil	
	A River Scene, with a Hut on an Island NG 154 Oak panel	1640–5	1. White highlight of cloud	Heat-bodied linseed oil	

DUTCH SCHOOL (continued)

Artist	Picture	Date	Sample	Medium	Note
Jacob van **Ruisdael**	*A Road winding between Trees towards a Distant Cottage* NG 988 Oak panel	probably 1645–50	1. Pale blue sky, top centre	Linseed oil	
Jan **Steen**	*A Young Woman playing a Harpsichord to a Young Man* NG 856 Oak panel	probably 1659	1. Buff-coloured paint of floor, right-hand side	Heat-bodied linseed oil	
			2. Discoloured blue-grey of patterned wall-hanging	Heat-bodied linseed oil	
			3. Bright blue of dress	Heat-bodied linseed oil	
	Skittle Players outside an Inn NG 2560 Oak panel	probably 1660–3	1. Blue-green leaf	Heat-bodied linseed oil	
			2. Buff paint of soil, lower right-hand corner	Heat-bodied linseed oil	
Jan **Wijnants**	*A Landscape with Two Dead Trees, and Two Sportsmen with Dogs on a Sandy Road* NG 972 Oak panel	probably 1665–75	1. Blue sky, top edge	Heat-bodied linseed oil	
Jan van **Huysum**	*Hollyhocks and other Flowers in a Vase* NG 1001 Canvas	1702–20	1. Brown paint of table's edge	Linseed oil	
			2. Dark greenish blue of leaves, lower right	Linseed oil	
			3. Pure white of edge of central	Heat-bodied walnut oil	
			4. Dark yellow toning glaze over paler green paint of leaf	Linseed oil	
			5. Blue 'highlight' of blue-green leaf in shadow of blue leaf	Heat-bodied walnut oil	
	Flowers in a Terracotta Vase NG 796 Canvas	1736–7	1. Pure white of flower, left-hand side	Walnut oil	
			2. Mid-green of leaf, upper right-hand side	Linseed oil	
			3. Yellow glaze on green leaf at bottom edge	Linseed oil	
Jan van **Os**	*Fruit, Flowers and a Fish* NG 1380 Mahogany panel	1772	1. Mustard-coloured impasto of outline of skin-segment of pomegranate	Heat-bodied linseed oil	
			2. Pure white highlight of central rose	Poppyseed oil	
			3. Brown background, left-hand edge	Heat-bodied linseed oil	
	Fruit and Flowers in a Terracotta Vase NG 6520 Mahogany panel	1777–8	1. Dark red glaze paint of peony	Linseed oil + pine resin	This sample was thick and had a heavy craquelure

FRENCH SCHOOLS

Artist	Picture	Date	Sample	Medium	Note
Nicolas **Poussin**	*The Adoration of the Golden Calf* NG 5597 Canvas, laid down on board	by 1634	1. Brown of earth, lower centre	Linseed oil	
			2. Green of dress, central figure	Linseed oil	
			3. Mustard colour of leg, central male figure	Linseed oil[54]	
Sébastien **Bourdon**	*The Return of the Ark* NG 64 Canvas	perhaps 1659	1. Warm white highlights of clouds, left edge	Heat-bodied walnut oil	Thick paint
			2. Greenish-grey repaint in sky (top edge)	Linseed oil + pine resin + trace copaiba	Notably richer in texture than sample 3[55]
			3. Original sky paint (blue-grey), top edge	Heat-bodied walnut oil	
François-Xavier **Fabre**	*Italian Landscape* NG 6564 Canvas	1811	1. Dark brown tree trunk, lower left-hand edge	Linseed oil	
			2. Green leaf of clinging ivy from same tree-trunk	Linseed oil	
Jean-Baptiste-Camille **Corot**	*The Roman Campagna, with the Claudian Aqueduct* NG 3285 Paper, laid down on canvas	probably 1826	1. Blue sky, slight impasto	Heat-bodied linseed/walnut oil + minor addition of pine resin	7-oxodehydroabietic acid identified by GC–MS P/S ratio = 2.0
			2. Green impasto of bank	Heat-bodied linseed oil + a trace only of pine resin + trace of mastic resin, both within the paint	Pine resin identified from the presence of 7-oxodehydroabietic acid; moronic acid indicated the presence of mastic resin, using GC–MS
	The Seine near Rouen NG 4181 Canvas	probably 1830–5	1. Pale blue-grey sky from under edging paper	Heat-bodied walnut oil	
			2. Blue-green of distant hills	Heat-bodied walnut oil	
	Avignon from the West NG 3237 Canvas	probably 1836	1. Blue sky, near top edge	Heat-bodied walnut oil	
	Monsieur Pivot on Horseback NG 3816 Canvas	*c.*1850–5	1. Greyish-blue underlayer, below green background, right-hand edge at damage	Heat-bodied walnut oil + minor addition of pine resin	Trace of pine resin identified by the presence of 7-oxo-dehydroabietic acid
			2. Thin unpigmented layer, above sample 3	Drying oil	This sample was too small for GC–MS, but FTIR–microscopy indicated it to be a drying oil layer, probably representing an 'oiling out'
			3. Dark green background paint over sample 1, after removal of varnish and 'oiling out' layer	Heat-bodied walnut oil + a little pine resin	

FRENCH SCHOOLS (continued)

Artist	Picture	Date	Sample	Medium	Note
Jean-Baptiste-Camille Corot (continued)	*The Leaning Tree Trunk* NG 2625 Canvas	*c.*1855–60	1. White of sky, to the right of the bent tree	Heat-bodied walnut oil	
			2. Pale blue sky	Walnut oil	
			3. Green paint, right-hand edge	Walnut oil[56]	
	The Oak in the Valley NG 6466 Canvas	1871	1. Green grass of foreground, bottom edge turnover	Heat-bodied poppyseed oil + some pine resin + some copal	
			2. Ground layer beneath sample 1	Heat-bodied linseed/walnut oil (probably the former) + trace of pine resin + trace of beeswax	
			3. White impasto of cloud	Heat-bodied poppyseed oil + very small amount of pine resin	
	Souvenir of Palluel NG 6467 Canvas	1871	1. Pale blue sky, left-hand edge	Heat-bodied walnut oil + possibly a trace of pine resin	
			2. Light grey-green, left-hand edge	Heat-bodied walnut oil + a trace of pine resin	
	Landscape at Arleux-du-Nord NG 6531 Canvas	1871–4	1. Brighter green of water, bottom edge	Heat-bodied walnut oil + trace of copaiba-like resin	It is possible that this brighter green was added later: compare with the duller green of sample 2
			2. Dull green water	Linseed oil + trace of pine resin	
			3. White impasto of cloud	Heat-bodied poppyseed oil + minor addition of pine resin; no copal detected	
	Evening on the Lake NG 2627 Canvas	*c.*1872	1. Darker green of foliage of trees, upper right-hand side	Heat-bodied walnut oil + a little mastic resin (moronic and a little oleanonic acids present) and copal (agathic acid) in the paint[57]	
Follower of Corot	*Seascape with Figures on Cliffs* NG 6416 Canvas	1865–75	1. Green grass	Linseed or walnut oil, probably the former, partially heat-bodied[58]	
			2. Blue sky	Linseed oil, partially heat-bodied	
			3. 'Warm' white impasto	Partially heat-bodied linseed oil + agathic acid-containing copal[59]	

FRENCH SCHOOLS (continued)

Artist	Picture	Date	Sample	Medium	Note
Jean-Désiré-Gustave **Courbet**	*Self Portrait (L'Homme à la Ceinture de Cuir)* NG 3240 Millboard	1845–50	1. Brownish-black drape in background	Heat-bodied walnut oil	
			2. Dull blue-green under-paint, above ground	Heat-bodied walnut oil[60]	
			3. Brownish black (from background) with red-translucent areas mixed	Heat-bodied walnut oil	
			4. Greenish-grey underpaint from exposed area, left-hand edge	Heat-bodied walnut oil	
			5. Ground layer from beneath sample 4	Linseed oil	
			6. Black background, left-hand edge	Heat-bodied walnut oil	
			7. Black background, lower layer from inside crack	Heat-bodied walnut oil – relatively rich compared to sample 6; also some camphor detected by GC–MS[61]	
	Beach Scene NG 6396 Canvas	1874	1. White impasto highlight of rock	Linseed oil	GC only
			2. Blue-grey sea, left-hand edge	Linseed oil	GC only
After **Courbet**	*The Sea near Palavas* NG 2767 Canvas	1850–1900	1. Sand-coloured paint of shore, left-hand edge	Poppyseed oil + traces of copal	
			2. Pale blue sea, left-hand edge	Poppyseed oil + traces of copal[62]	
Charles-François **Daubigny**	*The Garden Wall* NG 2624 Oak (?) panel	1860–78	1. Pale blue sky	Linseed oil	FTIR and GC only
	Alders NG 2623 Mahogany (?) panel	1872	1. Ground from edge, left-hand side	Heat-bodied linseed oil	
			2. Mid-blue-grey sky above horizon	Heat-bodied linseed oil	
			3. Dark green paint of foliage, left-hand foreground	Heat-bodied poppyseed oil + pine resin + copal	Very hard, glossy paint
	Landscape with Cattle by a Stream NG 6324 Wood panel	1872	1. Dark olive-green impasto of grass in foreground	Walnut oil + a little pine resin + dammar resin	During sampling the paint appeared to be very brittle
			2. Orange sunset	Walnut oil + a little pine resin	Not as brittle as sample 1
	St Paul's from the Surrey Side NG 2876 Oak (?) panel	1873	1. Cream impasto stroke of highlight in distance between posts	Heat-bodied linseed oil + a little pine resin	

FRENCH SCHOOLS (continued)

Artist	Picture	Date	Sample	Medium	Note
Charles-François **Daubigny** (continued)	*View on the Oise* NG 6323 Wood panel	1873	1. White sky paint, right-hand side	Walnut oil	
			2. Glossy green foliage, right-hand side	Heat-bodied linseed oil + some fir balsam	
			3. Grey-black paint from reverse	Walnut oil, rich in pigment, lean in medium	Very dry and hard
	Willows NG 2621 Canvas	probably 1874	1. Cream highlight impasto of cloud, upper right-hand side	Linseed oil	
			2. Dark, bottle-green impasto stroke of vegetation under trees, right-hand side	Heat-bodied walnut oil + a little dammar resin	
Narcisse-Virgilio **Diaz** de la Peña	*Common with Stormy Sunset* NG 2633 Mahogany (?) panel	1850	1. Olive-green sky paint, left-hand edge	Heat-bodied walnut oil + moderate amount of fir balsam	7-oxodehydroabietic acid + norambreinolide type components (B^+ = 123/M^+ = 250); quite hard, brittle, glossy paint
			2. Deep green foliage, right-hand edge	Heat-bodied walnut oil + fir balsam	FTIR–microscopy picked out drying oil bands at 1776 cm^{-1}, but terpenoid lactone bands were obscured by the oil bands; glossy paint
			3. Pale blue sky, right-hand edge	Walnut oil, heat-bodied, but less so than above; trace only of fir balsam, in comparison with samples 1 and 2	Sample 3 was noticeably less glossy than samples 1 and 2
	Sunny Days in the Forest NG 2058 Canvas	probably 1850–60	1. White highlight impasto paint of rock in foreground	Heat-bodied walnut oil with traces of copal (agathic acid)	
			2. Blue sky paint	Walnut oil	
	The Storm NG 2632 Mahogany panel	1871	1. Olive-green grass, left-hand edge	Heat-bodied walnut oil + fir balsam + a trace of agathates from a copal[63]	
			2. Yellowish-white impasto of sunlit path	Heat-bodied walnut oil	
Attributed to **Diaz**	*Cows at a Pool* NG 4579 Mahogany (?) panel	1840–76	1. White impasto from sky	Walnut oil	
Jules-Louis **Dupré**	*Willows, with a Man Fishing* NG 2634	probably before 1867	1. Pale blue sky, top edge	Poppyseed oil	
			2. Dark, bottle-green foliage of foreground	Heat-bodied poppyseed oil	
Pierre-Etienne-Théodore **Rousseau**	*Sunset in the Auvergne* NG 2635 Wood panel	1830	1. Pale yellow impasto of sunset	Walnut oil	GC analysis only
			2. Rich dark brown paint of trees, mid-left	Heat-bodied linseed oil with some pine resin	

FRENCH SCHOOLS (continued)

Artist	Picture	Date	Sample	Medium	Note
Pierre-Etienne-Théodore **Rousseau** (continued)	*The Valley of St-Vincent* NG 3296 Paper, laid down on canvas	probably 1830	1. Olive-green landscape, right-hand edge	Heat-bodied linseed oil	
			2. Blue-grey of distant hill, right-hand edge	Heat-bodied walnut oil	
	A Rocky Landscape NG 4170 Millboard	*c.*1836–40	1. Blue sky	Walnut oil	GC analysis only
	River Scene NG 2439 Oak(?) panel	*c.*1840–60	1. Pale bluish-green sky	Heat-bodied linseed oil + a trace of pine resin	7-oxodehydroabietic acid detected by GC–MS
			2. Dark brownish-green foliage, left-hand side	Heat-bodied linseed oil + a little pine resin	
	Landscape NG 5781 Millboard	probably 1860–5	1. White sky paint	Heat-bodied walnut oil (trace of copal resin present)	This was sampled from a well-defined brushstroke
			2. Brown brushstroke of foreground branch	Heat-bodied linseed oil + a little mastic	Glossy paint, at surface; no copal detected in this sample
			3. Transparent glaze over brown paint (sample 2), as if simulating a shadow under the trees on left	Heat-bodied walnut oil + mummy(?) + a trace of copal resin[64]	
			4. Mid-blue sky	Heat-bodied walnut oil + a trace of copal[65]	
Gustave **Moreau**	*Saint George and the Dragon* NG 6436	1889–90	1. Red lake paint of drape on horse	Heat-bodied walnut oil	No conifer resin but a component suggesting the presence of a Leguminosae copal resin was observed
			2. White impasto of horse's head, below eye	Heat-bodied walnut oil	
			3. Black impasto of background, upper left	Heat-bodied walnut oil detected by GC only	GC–MS indicated the same heat-bodied oil, but some copal present too
			4. Blue impasto of highlight of pool of water in foreground, lower right	Heat-bodied walnut oil	GC only
Hilaire-Germain-Edgar **Degas**	*Hélène Rouart in her Father's Study* NG 6469 Canvas	*c.*1886	1. Pale powder blue of frame of vitrine	Poppyseed oil	
			2. Brown-red of upper wall in background	Heat-bodied walnut oil or a mixture of linseed and poppyseed oils	
			3. Bright orange outline stroke, right shoulder	Drying oil	FTIR only; from its surface appearance this was widely assumed to be pastel
			4. Thin black brushstroke on sitter's left lace cuff	Partially heat-bodied linseed oil	

SPANISH SCHOOL

Artist	Picture	Date	Sample	Medium	Note
Diego **Velázquez**	*Saint John the Evangelist on the Island of Patmos* NG 6264 Canvas	*c.*1618	1. Red outline of pale pink of cloak, draped over Saint John's lap	Heat-bodied linseed oil	
			2. Cool white highlight of Saint John's sleeve	Heat-bodied linseed oil	
			3. Black outline paint of Saint John's robe	Heat-bodied linseed oil, lean in medium, rather open-textured paint	
	The Immaculate Conception NG 6424 Canvas	*c.*1618	1. Dark blue cloak of the Virgin, from a fold	Heat-bodied linseed oil	
			2. White of cloud	Heat-bodied linseed oil	
			3. Dark brown, thick 'daubs' of paint of leaves of tree	Heat-bodied linseed oil	
			4. Brown ground exposed in modelling of sky	Linseed oil	
			5. Red lake paint of shadow of a fold in Virgin's sleeve	Heat-bodied linseed oil	

GERMAN SCHOOL

Artist	Picture	Date	Sample	Medium	Note
Jacob **Weier**	*Cavalry attacked by Infantry* NG 1470 Oak panel	1645	1. Grey sky, top edge	Linseed oil, rather lean	

BRITISH SCHOOL

Artist	Picture	Date	Sample	Medium	Note
Thomas **Gainsborough**	*John Plampin* NG 5984 Canvas	*c.*1755	1. Mid-green grass of bank, right-hand edge	Heat-bodied linseed oil	
			2. Thick brownish-green paint of distant trees	Heat-bodied linseed oil	
			3. Light brown layer below sample 2 – seemingly ground	Linseed oil, partially heat-bodied	
			4. Yellow highlight of clouds	Heat-bodied walnut oil	
John **Constable**	*The Hay-Wain* NG 1207 Canvas	1821	1. White impasto of highlight of cloud	Heat-bodied walnut oil	
			2. Mid-blue sky paint, right-hand edge	Linseed oil, partially heat-bodied	
			3. Thick mid-green foliage on grassy bank, left-hand side	Heat-bodied linseed oil	