



# NATIONAL GALLERY TECHNICAL BULLETIN

VOLUME 28, 2007

National Gallery Company  
Limited

Distributed by  
Yale University Press

This volume of the *Technical Bulletin* has been funded by the American Friends of the National Gallery, London with a generous donation from Mrs Charles Wrightsman.

Series editor Ashok Roy

© National Gallery Company Limited 2007

All rights reserved. No part of this publication may be transmitted in any form or by any means, electronic or mechanical, including photocopy, recording, or any information storage and retrieval system, without the prior permission in writing of the publisher.

First published in Great Britain in 2007 by  
National Gallery Company Limited  
St Vincent House, 30 Orange Street  
London WC2H 7HH

[www.nationalgallery.co.uk](http://www.nationalgallery.co.uk)

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

ISBN 978 1 85709 357 5  
ISSN 0140 7430  
525049

Publisher Kate Bell  
Project manager Jan Green  
Editor Diana Davies  
Designer Tim Harvey  
Picture research Suzanne Bosman  
Production Jane Hyne and Penny Le Tissier  
Repro by Alta Image, London

Printed in Italy by Conti Tipocolor

FRONT COVER

Claude-Oscar Monet, *Iris* (NG 6383), detail of PLATE 2,  
page 59.

TITLE PAGE

Bernardo Daddi, *Four Musical Angels*, Oxford, Christ Church,  
detail of PLATE 2, page 5.

### **Photographic credits**

All photographs reproduced in this *Bulletin* are  
© The National Gallery, London, unless credited  
otherwise below.

#### ALTENBURG/THÜRINGEN

##### **Lindenau Museum Altenburg**

© Lindenau Museum Altenburg. Photo Sinterhauf:  
p. 21, pl. 28; p. 22, pl. 29

#### BRADFORD

##### **Society of Dyers and Colorists**

© Photo courtesy of the Society of Dyers and Colorists:  
p. 69, pl. 1

#### CAMBRIDGE

##### **Fitzwilliam Museum, Cambridge**

© The Fitzwilliam Museum, University of Cambridge:  
p. 22, pl. 30

#### EDINBURGH

##### **Duke of Sutherland Collection, on loan to the National Gallery of Scotland, Edinburgh**

© National Galleries of Scotland: p. 41, pl. 7

##### **National Gallery of Scotland**

© National Galleries of Scotland: p. 43, pl. 10

#### FLORENCE

##### **Galleria dell'Accademia**

© Photo Bridgeman Art Library, London: p. 8, pl. 6

##### **Santa Croce, Florence**

© Photo Bridgeman Art Library, London: p. 8, pl. 5

#### LONDON

##### **British Museum**

© The British Museum: p. 38, fig. 2

##### **Christie's Images, London**

© Courtesy Christie's Images, London: p. 16, fig. 5

##### **The Royal Collection**

The Royal Collection © 2006, Her Majesty Queen  
Elizabeth II: p. 7, pl. 3

#### MADRID

##### **Museo Nacional del Prado, Madrid**

© Bridgeman Art Library, London: p. 38, pl. 4

© Museo Nacional del Prado, Madrid: p. 39, pl. 6

#### PARIS

##### **Durand-Ruel**

© Archives Durand-Ruel: p. 60, fig. 2

© Archives Durand-Ruel, droits réservés: p. 60, fig. 1

##### **Musée du Louvre, Paris. Cabinet des Dessins**

© RMN, Paris. Photo Jean-Gilles Berizzi: p. 34, pl. 3

#### SAN FRANCISCO

##### **Fine Arts Museums of San Francisco, California**

© Fine Arts Museums of San Francisco, California: p. 45, fig. 6

#### SIENA

##### **Pinacoteca Nazionale, Siena**

© The Art Archive, London: p. 16, pl. 19

#### ST PETERSBURG

##### **The State Hermitage Museum, St Petersburg**

© With permission from The State Hermitage Museum,  
St Petersburg: p. 30, pl. 2

#### STAMFORD

**Burghley House:** p. 39, pl. 5

#### WASHINGTON, DC

##### **National Gallery of Art, Washington, DC**

© National Gallery of Art, Washington, DC. Image 2006  
Board of Trustees: p. 38, pl. 3

# The Technology of Eighteenth- and Nineteenth-Century Red Lake Pigments

JO KIRBY, MARIKA SPRING AND CATHERINE HIGGITT

THE EIGHTEENTH and nineteenth centuries saw a huge expansion in the use of and demand for natural dyes, in parallel with considerable technological developments in the textile industry. The stimulus for this had its roots in the seventeenth century, with the import of printed cotton fabrics from India. Locally produced cotton calicoes, *indiennes*, based on the Indian models, became hugely popular across Europe, and although this prompted some resistance and legal restrictions in favour of the wool and silk industries in some countries, in others, notably the Netherlands, cotton dyeing and printing became an important industry. By the late eighteenth century, with the relaxation of the legal restraints, processes for producing textiles were becoming industrialised and very much more complex. In England, for example, the production of cotton cloths became mechanised from the late 1770s, which enabled a very much more efficient production of the final fabric. It is thus no surprise to learn that England had become the dominant producer of printed cottons by the early nineteenth century.<sup>1</sup> At the same time, the growth in the textile industry was one factor stimulating the development of methods to satisfy the growing need for alkalis and other chemicals: that is, the beginnings of the modern chemical industry.<sup>2</sup>

The need to meet the ever-increasing demand for printed cottons necessarily led to a greatly increased demand for dyestuffs, notably madder, *Rubia tinctorum* L., which could give a bright fast red on cotton. Another stimulus for the cultivation of madder was the desire to find an alternative source of red to the heavily used New World cochineal insect, *Dactylopius coccus* Costa, the import of which was a highly lucrative Spanish monopoly.<sup>3</sup> Only in 1777 were some of the precious insects obtained by subterfuge by the Frenchman Nicolas Thierry de Menonville, who tried to establish them in Santo Domingo (now Haiti). This experiment was short-lived, but later attempts were made to establish plantations of the nopal cactus and the insects in Spain itself and in southern France. Colonies were later established in other parts of the world, including the Canary Islands (by Spain),

Algeria (by France) and Java (by the Dutch, using Spanish stock obtained from Cádiz by industrial espionage). In the early decades of the nineteenth century, other Central American countries such as Peru, Guatemala, Bolivia and Chile also took advantage of the crumbling state of the Spanish empire and developed their own cochineal export industries.<sup>4</sup>

The search for a method to reproduce the bright red madder colour seen on imported fabrics, the so-called Turkey red (PLATE 1), and the need to produce dyestuff in such a form that efficient printing could be carried out stimulated research into methods of processing the madder root for efficient dye extraction and the chemistry of the madder dye. The colouring matter of the cochineal insect was studied for similar reasons.

These developments in the understanding of the chemistry of the dyestuffs inevitably had an influence on the production methods for red lake pigments where the colouring matter originated from natural dyestuffs. Not only might the dyestuff itself be processed differently, but also the methods and some of the ingredients used to prepare the pigment were slightly different to those used earlier. Traditionally the alkali used had often been a solution of potassium carbonate, potash, made from wood ash. By the late



PLATE 1 Example of Turkey red dyeing on cotton, from Paul Schützenberger, *Traité des matières colorantes, comprenant leurs applications à la teinture et à l'impression*, Paris 1867, Vol. 2, p. 290 (Echantillon 13).

eighteenth century, the need for alkali had reached a level where it could no longer be met from plant sources: a synthetic process was thought necessary. The Leblanc process, whereby sodium carbonate was obtained from common salt by treating it with sulphuric acid and roasting the sodium sulphate formed with limestone and coal, was devised in response to a competition set by the French government in 1775 and won by Nicolas Leblanc in 1790.<sup>5</sup> The process became standard by the mid-nineteenth century and this is reflected in frequent references to soda or sodium salts as ingredients in nineteenth-century recipes for lake pigments, rather than the potassium salts of the eighteenth century.

Changes in the recipes might also lead to differences in the composition of the substrate of red lakes. For example, it has been found that the preparation of amorphous hydrated alumina by the addition of alkali to alum, as became common practice by the late eighteenth century, rather than by the addition of alum to an alkaline solution of the dyestuff, the general practice earlier, results in the incorporation of sulphate ions brought down during the precipitation. The result is a substrate rather similar to the light alumina hydrate described in modern paint technology literature.<sup>6</sup>

Examination of red lake pigments used in eighteenth- and nineteenth-century paintings in the National Gallery Collection, presented in Tables 1a and 1b, confirms the influence these developments had on their composition. The paintings studied for this survey were all examined during previous conservation treatment or for the preparation of National Gallery Schools catalogues. For the present investigation, paint samples were examined by optical microscopy, energy dispersive X-ray microanalysis in the scanning electron microscope (SEM-EDX), and Fourier transform infrared (FTIR) microscopy and spectroscopy. High-performance liquid chromatography (HPLC) was used to analyse the dyestuffs wherever possible. The results show the wide use of cochineal and madder to prepare pigments, as is perhaps to be expected since they were so heavily used and so intensively researched. Other dyestuffs used in earlier periods for pigment preparation, such as brazilwood, *Caesalpinia* spp., and lac dye, produced, together with the resin-like shellac, by the Indian lac insect *Kerria lacca* (Kerr) and other species, were still in use, but they seem to have had a limited application in the preparation of pigments for artists. This is also true of the new, brilliantly coloured, so-called coal tar dyes, although these came to be widely used for other purposes.

## Cochineal

The two principal regions of Central and South America where cochineal was to be found were the Peruvian Andes and Mexico – New Spain. The active cultivation of the insect for dyeing and as a source of pigment was already well established in Mexico when the Spanish arrived and this country was the principal source of the cochineal available in Europe until the end of the eighteenth century. Usable quantities probably first arrived in Spain in the 1520s; it was used for dyeing in Florence in 1542, Venice in 1543 and is said to have been in demand in Antwerp by 1550.<sup>7</sup> It was available in London by the 1560s.

Cochineal was an unusual commodity in that both farmed – *finá* – and wild – *silvestre* – varieties were used (the smaller wild insects making up the *silvestre* product perhaps including other local *Dactylopius* species), but the *finá* form was that destined for export. Apart from precious metals, cochineal was one of the most valuable and substantial export commodities. Quantities exported were very variable; this was a labour-intensive industry and could be affected by factors such as poor harvest of other crops and adverse climatic conditions, thus some periods were very lean. At other times, however, amounts were substantial.<sup>8</sup>

During the sixteenth century, when the New World dyestuff first came into use, and for many decades subsequently, cochineal lake pigments were prepared by the method used for lakes containing kermes and Old World cochineal dyes: that is, by extracting the dyestuff from dyed textile shearings using alkali and adding alum to precipitate the dyestuff on a substrate of amorphous hydrated alumina. These lakes have been identified in several paintings in the National Gallery Collection, including Joachim Beuckelaer's *The Four Elements: Air, A Poultry Market with the Prodigal Son in the Background* (NG 6587), painted in Antwerp in 1570, and Eustache Le Sueur's *Alexander and his Doctor* (NG 6576), of about 1648–9. In both these cases, the dyestuff was probably extracted from silk shearings: examination by HPLC revealed the presence of a little ellagic acid, probably derived from galls used to weight the silk before dyeing.<sup>9</sup>

At the end of the sixteenth century and beginning of the seventeenth, three developments occurred which changed the method of making cochineal pigments fundamentally. In 1612, Antonio Neri published an influential treatise on glass making, *L'arte vetraria*, which also contained some pigment recipes. Two of these were for making lake pigments from *chermesi*, a name that then signified crimson, and an Old or New World cochineal insect. In the first, the

insects were used to dye wool, but the dyestuff was then re-extracted with alkali and precipitated with alum. The second, a method invented by Neri in Pisa, was more significant: the dyestuff was extracted from the insects with alcohol and an aqueous solution of alum was added to precipitate the pigment; the dyed textile stage was by-passed.<sup>10</sup>

The second development was the discovery of a method of precipitating the insect dyestuff, predominantly carminic acid, which is present in the insect as the potassium compound,<sup>11</sup> in the form of a metal complex or salt. The resulting pigment lacks the high proportion of hydrated alumina substrate present in a conventional cochineal lake and became known as carmine. The preparation is feasible because the amount of dyestuff contained by the Mexican cochineal insect is as much as 19 or 20% by weight,<sup>12</sup> about ten times that contained by the kermes insect, *Kermes vermilio* Planchon, and considerably more than the Old World sources of carminic acid, *Porphyrophora* spp. The discovery was, apparently, a matter of chance. The story is told that, in the 1580s, a Franciscan monk in Pisa making a pharmaceutical preparation with an extract of cochineal and cream of tartar (potassium hydrogen tartrate) inadvertently added acid, making the remedy unusable. It was set aside and after a few days a red precipitate formed. The story continues that a painter found this served well as a pigment and requested that it be made again.<sup>13</sup> A recipe for the preparation of cochineal carmine, boiling the cochineal with a little kermes, alder (bark, perhaps) and potash alum, filtering off the liquid and leaving it to stand for the carmine to settle out, is said to have been published in 1656 (Table 2).<sup>14</sup> Whether or not it is coincidental that both these advances took place in Pisa within about twenty years of one another (Neri was working in Pisa between 1601 and 1603), it is the case that recipes for cochineal (and kermes) pigments quite unlike those of earlier times begin to appear. A mid-seventeenth-century Italian source, for example, includes a direct method, dissolving the dyestuff in alkali and precipitating the lake with alum; another consists of adding alum to a solution of the dyestuff in an extract of fennel seed. 'Carmine colour' is made by adding arsenic crystals to an alkaline solution of the dyestuff.<sup>15</sup>

By the end of the seventeenth century, carmine is recorded as being used for miniature painting; it was generally too expensive for easel painting.<sup>16</sup> It was made by boiling the ground cochineal in water previously boiled with the astringent seeds of *chouan*, *Anabasis tamariscifolia* L., adding a little potash alum, allowing the insect matter to settle out, decanting off

the red liquid and leaving it to stand until the carmine settled out. As Table 2 shows, there were various modifications of this method, which is said to have first appeared in 1656 and continued to be cited until the late nineteenth century.<sup>17</sup> Apart from any astringent property or tannin content the plant matters might contain that might aid precipitation, some also contained yellow or orange dyestuff, which would give a less blue crimson product. During the eighteenth century, other, more predictable methods, appeared. Some involved the addition of alum and cream of tartar, or alum alone, to the boiling cochineal mixture. The earliest examples seem to be found in mid-eighteenth-century German chemistry books and other sources;<sup>18</sup> the method with alum is in fact described in later French sources as 'the German method'.

The third development affecting the preparation of cochineal pigments was the introduction of tin salts in the mordanting and dyeing of wool and silk with cochineal; this resulted in a brilliant scarlet colour. Early in the seventeenth century, Cornelius Drebbel discovered that a solution of tin in aqua regia turned an aqueous solution of cochineal dye scarlet. The use of tin salts with cochineal to dye wool and silk scarlet was developed by his sons-in-law, the Kuffler brothers, in their London dyeworks at Bow and spread across Europe by the 1640s.<sup>19</sup> At some time during the first half of the eighteenth century, the same tin salts were used to precipitate carmine from cochineal solution; this was more scarlet than the crimson-coloured carmine produced by the use of alum and cream of tartar.<sup>20</sup> The English apothecary and chemist Robert Dossie observed in 1758 that there was a similarity between the preparation of carmine and dyeing, and earlier authors had wondered about a similar connection.<sup>21</sup> In parallel with this, authors writing on dyeing commented on the tendency of the salts formed by dissolving tin in aqua regia (giving tin[IV] chloride) or nitric acid (giving soluble tin nitrates with cold dilute acid, a form of tin[IV] oxide with concentrated acid) to precipitate in the dye bath, forming a sort of lake.<sup>22</sup> It thus seems highly likely that the tin-containing cochineals are linked with the technology of the dye bath. In later French recipe collections, the name 'Chinese' was associated with the tin[IV] chloride method.<sup>23</sup>

Carmine was very slow to precipitate and several recipes, first appearing in the late eighteenth century, suggest the addition of a solution of fish glue or beaten egg white in water to help bring it down; these recipes also generally use a little alkali with the alum to precipitate the carmine (see Table 2).<sup>24</sup> Pierre-Joseph Pelletier and Joseph-Bienaimé

Caventou, who isolated the colouring matter of cochineal in 1818, suggested that the use of a little alkali helped to dissolve out ‘animal matter’, the nature of which they were unable to clarify, associated with the dye; they thought the presence of the animal matter improved the yield of carmine obtained by the addition of acids or acid salts (including alum and cream of tartar). Inevitably, however, the reaction between alkali and alum would bring down the dyestuff in a form more like a deeply coloured hydrated alumina-containing lake than a ‘true’ carmine. In fact, Pelletier and Caventou discovered that many pigments sold as carmines by Paris colour merchants contained alumina (they also discovered that some contained vermilion).<sup>25</sup> Nevertheless, this method was one of those tried by J.F.L. Mérimée, who cited Pelletier and Caventou’s work as his source, and modifications of it were used by others.<sup>26</sup> A sample of carmine from a collection of pigments from J.M.W. Turner’s studio, now in the possession of Tate Britain, London, was found to be of this type; under the microscope it had the appearance of a very deeply coloured purplish-red lake pigment of relatively small particle size.<sup>27</sup>

The methods of preparation were sometimes misunderstood. For example, to make carmine the editors of the *Encyclopédie raisonnée* recommended a recipe from Johann Kunckel’s 1679 German edition of Neri’s work: Neri’s recipe for preparing cochineal lake by dyeing wool and re-extracting the colour. This led Robert Dossie to comment:

The compilers of the new French Cyclopedia have given two or three old recipes for the preparation of this colour; and afterwards recommended another; which on examination is only a process for making bad lake of scarlet rags: but rather than to insert such imperfect instructions for the making of an article of great consequence ... I chuse to be silent, and acknowledge my own ignorance in this particular ...<sup>28</sup>

While Dossie accepted that the best, most durable, carmine was prepared in France, he disagreed with the suggestion that this was due to ‘some qualities in the air and water’. In fact, up to the end of the nineteenth century, most sources gave the impression that the making of carmine was an art, requiring the best cochineal, iron-free alum, the purest water, the cleanest vessels of porcelain, glass or well-tinned copper and a sunny day: Philippe de la Hire commented that it was impossible to make in cold weather as it would not precipitate and the liquid gelled and went bad.<sup>29</sup>

Over a century later, an Austrian author commented that it was impossible to obtain a good product in England because of the weather.<sup>30</sup>

It is clear that a good carmine was not easy to make. The early nineteenth-century English colour-maker George Field (1777–1854), in notes on experiments carried out on the permanence of pigments – his own and many made by other London colourmen – during the first quarter of the nineteenth century, described a carmine made by a Mr R. Hancock Senior in 1792 as ‘the most successful of his attempts, more red than carmine’, which suggests that other carmines were less successful.<sup>31</sup> Study of the surviving archives of English colourmakers such as Lewis Berger and Company Ltd and Winsor & Newton shows that they devoted a great deal of attention to the making of carmines, with many trials.<sup>32</sup> Lewis Berger was making carmines by the 1770s (the early ones appear to have contained vermilion, clearly a fairly common practice) and these, together with cochineal lakes, remained an important part of his company’s range throughout the nineteenth century. They supplied other colourmakers; Winsor & Newton studied the Berger carmines quite closely,<sup>33</sup> and the recipes they used were similar. Over this period both companies used versions of the recipes discussed above: alum and cream of tartar, or, later, citric acid; alum with a mild alkali (borax, sodium borate); the use of milk, or other sources of protein (as in Table 2) to improve the yield. Berger used citric acid and milk from the 1830s to produce so-called Orient Carmine, a colour also made by Winsor & Newton, and tried the addition of a little ‘Nitro-Muriate’ of tin (tin[IV] chloride).<sup>34</sup> George Field, with whom Henry Newton (1805–1882) had worked, tried tin salts with cochineal to obtain a scarlet colour and Henry Newton himself, writing in 1840, noted that the addition of hydrated tin oxide to carmine (made by one of the other methods) increased the weight of the product without much affecting the colour. He also speculated that contemporary French carmines might contain a tin salt as they were much heavier than English carmines. Tin oxide had the added advantage of apparently protecting the pigments against mould formation.<sup>35</sup> Winsor & Newton did make a tin-containing ‘French Carmine’,<sup>36</sup> but neither Berger nor Winsor & Newton made or sold the number of carmines produced by French colourmakers in the mid-nineteenth century: Jules Lefort wrote in 1855 that there were at least twelve, the number given in a slightly later catalogue of the Paris colour merchants Lefranc et Cie, at prices ranging from 120 francs a kilogram

for the finest, Nacarat carmine, to 30 francs a kilogram for the lowest, grade 6, as '*couleurs en nature*'.<sup>37</sup>

As Pelletier and Caventou discovered, the methods of preparation involve making the pH of the cochineal extract slightly acidic – this includes Madame Cenette's method using oxalic acid (see Table 2).<sup>38</sup> Carmines prepared in the laboratory following recipes of the type listed in Table 2, using alum and cream of tartar, or alum alone, were precipitated at a pH of about 5, little different to that of an aqueous solution of carminic acid. The yield from carmine preparations was very low, which probably explains the high proportion of insects used, far higher than would be needed for a conventional lake. Comparison of the proportions of the ingredients, shown in Table 2, suggests that a slightly higher amount of the insects (compared to that of alum) was used in the alkali/alum methods than in the alum/cream of tartar methods (Wood's method of 1856 is unlike the others in this respect), and considerably more insects with the tin salts methods, although the reason for this is unclear. Tin[IV] chloride gave a much lower pH of about 2 and, as discussed above, a more scarlet carmine. Carminic acid shows marked changes in colour with pH, corresponding to different degrees of proton dissociation in the molecule.<sup>39</sup> The most marked change takes place over the pH region 4.8–6, for which it can be used as an indicator; here it shows a colour change from orange to crimson (mono-anion to di-anion conversion). Formation of scarlet tin-containing pigments takes place on the acid side of this pH range; aluminium-containing, more crimson carmines form more or less within it. Alumina-containing lakes tend to form on the alkaline side of this range and are a bluer crimson; indeed, as Pelletier and Cavantou observed, they can very easily become purple, particularly if heated.<sup>40</sup> As well as giving a more scarlet pigment, carmine recipes involving tin salts tend to yield greater amounts of pigment, largely because aqueous solutions of tin[IV] salts readily hydrolyse to an amorphous white hydrous tin[IV] oxide which precipitates,<sup>41</sup> bringing the dyestuff with it to produce a form of lake. Some eighteenth- and nineteenth-century recipes for cochineal lakes in fact consisted of adding tin salts to the cochineal solution to bring down most of the dyestuff and others involved adding a freshly made precipitate of a form of hydrated tin[IV] oxide to the dyestuff solution. These are less translucent than lakes on a substrate of hydrated alumina.

Modern carmine pigments are carminic acid complexes/salts of aluminium and calcium, and accounts in the modern pigment literature refer to

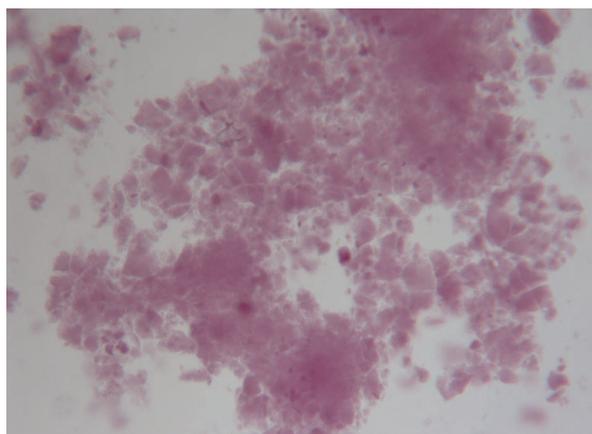


PLATE 2a Cochineal lake with a conventional hydrated alumina-type substrate. Dispersion, photographed by reflected light, 200x.

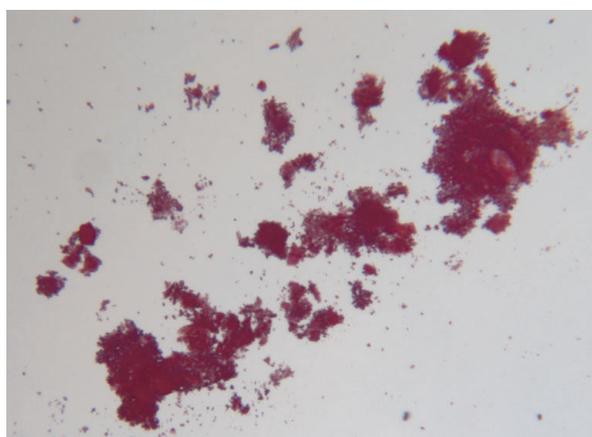


PLATE 2b Aluminium-containing carmine prepared in the laboratory. Dispersion, photographed by reflected light, 200x.

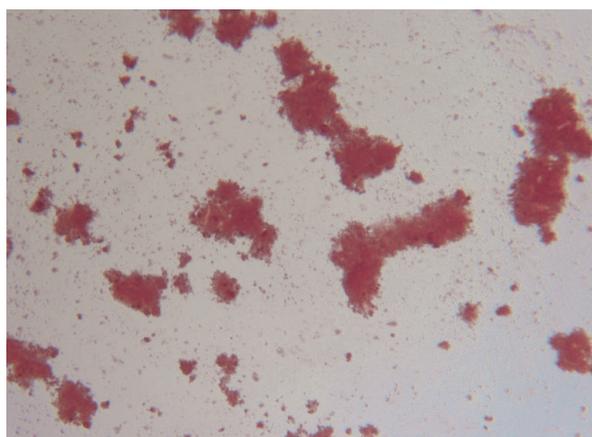


PLATE 2c Tin-containing carmine prepared in the laboratory. Dispersion, photographed by reflected light, 200x.

this variety.<sup>42</sup> However, the precise structure and composition are unclear. Bonding between the metal ion (Al, Ca or Sn) and the dyestuff molecule is likely to involve both salt and chelate formation (the latter



PLATE 3 Giovanni Battista Tiepolo, *An Allegory with Venus and Time* (NG 6387), c.1754–8. Canvas, 292 × 190.4 cm.

by way of one of the quinone oxygens and the adjacent hydroxyl group). The presence of the carboxylic acid group in carminic acid means that interaction between the metal ion and carboxylate function is also possible, as well as hydrogen bonding. The IR spectra of a variety of carmine pigments (Al-, Al/Ca- or Sn-containing), while showing close similarities to free carminic acid, demonstrate subtle variations in band intensity and position which may throw light on the bonding interactions.<sup>43</sup>

The appearance of a pure carmine under the microscope is very different from that of a conventional cochineal lake on a substrate of hydrated alumina, which has irregularly sized translucent cherry-red or pink particles (PLATE 2a). The carmines made in the laboratory have a very fine particle size and an extremely intense colour (PLATES 2b and 2c); their tinting strength would be very high and the seventeenth- or eighteenth-century painter would have found them very much stronger in colour than any other pigment then available, apart from the blue pigments indigo and, later, Prussian blue. In water-colour, carmine would be easy and economical to use

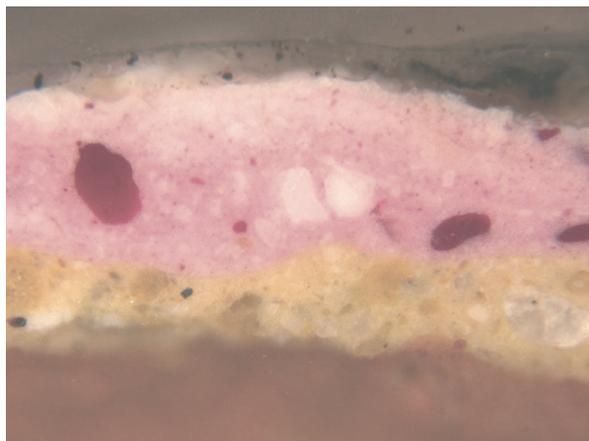


PLATE 4 Giovanni Battista Tiepolo, *An Allegory with Venus and Time* (NG 6387). Cross-section of a paint sample from the pink drapery of Venus. The uppermost pink layer contains lead white with some large particles of an intense red cochineal lake pigment on a sulphate-containing hydrated alumina substrate. Original magnification 200×, actual magnification 160×.

as a wash; in oil, apart from being very expensive, it would be very much easier to use with the addition of a translucent extender. This would reduce the intensity of the colour and bring it closer in its properties to other pigments: simply adding lead white would lighten the colour, but increase its opacity, which was not necessarily desirable. One can imagine that the amount of translucent extender added might determine whether the pigment would be sold as a carmine or a lake.

As only a limited amount of the dyestuff precipitated during a carmine preparation, lakes could be made from the colouring matter left in solution by adding tin salts as described above, or by adding freshly prepared alumina (the same methods are described for preparation of lake pigments even in those cases where no carmine was prepared). Alternatively, alum could be added to the dyestuff solution and alkali added to precipitate the pigment, or vice versa, or even some combination of these methods might be used. If tin salts were used as the precipitating agent, alumina, chalk, china clay or starch, or any combination of these, was often added.<sup>44</sup> In many cases, the resulting lake pigment could be described as a carmine with a great deal of extender.

In practice, during examination of the samples of cochineal-containing pigments listed in Tables 1a and 1b it was not always easy to make a distinction between a carmine and a lake pigment: in reality a continuum seems to have existed. Furthermore, in addition to the difficulty in deciding whereabouts on the carmine-cochineal lake continuum the pigment



PLATE 5 Giovanni Antonio Pellegrini, *Rebecca at the Well* (NG 6332), 1708–13. Canvas, 127.3 × 104.5 cm.

under investigation might lie, there is the question of under what name – carmine or lake – the pigment might have been sold and this is almost impossible to answer.

All the samples from eighteenth-century paintings examined during this study contained cochineal dyestuff (confirmed by HPLC or FTIR spectroscopy).<sup>45</sup> In some cases, the cochineal pigments were clearly conventional cochineal lakes very similar to those found in previous centuries. In a sample from the deep red chair back in Drouais's *Le Comte de Vaudreuil* (NG 4253) of 1758, SEM–EDX examination revealed the presence of aluminium, and small amounts of other elements such as potassium, sulphur, phosphorus, silicon, and calcium, which can originate from the scale insect dyestuff or the ingredients of the substrate (see Table 1a). FTIR microscopy confirmed the presence of a conventional hydrated alumina substrate. Pigments of this type continued to be made into the nineteenth century as can be seen from the pigment used for the executioner's red tights in Paul Delaroche's *The Execution of Lady Jane Grey* (NG 1909), dated 1833. However, in a number of the eighteenth-century works examined, such as *An Allegory with Venus and Time* (NG 6387) painted by Giovanni Battista Tiepolo in 1754–8 (PLATE 3), the high sulphur content of the lake pigment suggests a different method of manufacture to that used in previous

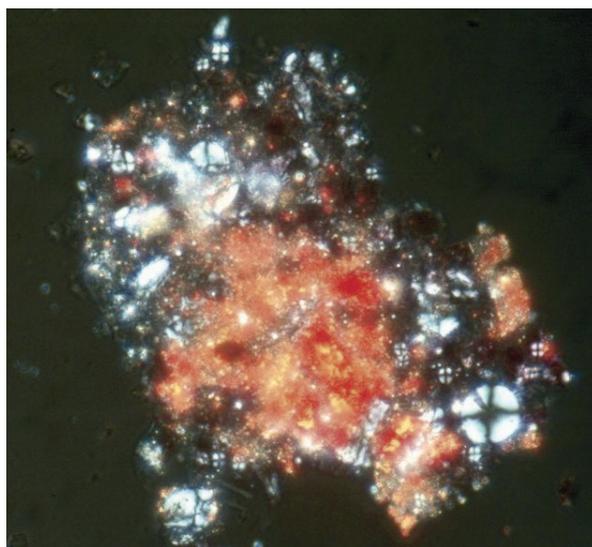


PLATE 6 Giovanni Antonio Pellegrini, *Rebecca at the Well* (NG 6332). Unmounted sample from the red cloak of the servant in transmitted light, cross polars. Large round particles, showing the dark cross characteristic of many types of starch grain when viewed under cross polars, are visible. Original magnification 400×, actual magnification 440×.

centuries (PLATE 4). In these cases the substrate is closer in composition to the light alumina hydrate of the nineteenth century.<sup>46</sup>

Although of similar appearance to the lakes described above by optical microscopy, EDX analysis showed that the pigment used for the red coat in *Lord Heathfield of Gibraltar* (NG 111), painted by Sir Joshua Reynolds in 1787, contained little aluminium. Bands are seen in the IR spectrum suggestive of the presence of a pigment rich in cochineal dyestuff, which may be interpreted as a carmine, but this is complicated by the presence of bands at  $\approx 1650$  and  $1550\text{ cm}^{-1}$  suggesting the presence of a significant amount of protein (it should be noted that the binder is oil). The presence of cochineal dyestuff extracted from wool shearings is unlikely; little or no sulphur is present.<sup>47</sup> It is more likely that a source of protein such as egg white or gelatine was added during the preparation of the pigment to aid precipitation: Table 2 shows several examples of this type of recipe. Several other similar examples were seen in paintings by Reynolds and Gainsborough, although these contained higher proportions of aluminium-based substrate.

Rounded, translucent inclusions with bluish fluorescence under ultraviolet (UV) illumination were observed in a large number of the cochineal-containing pigments examined, including three eighteenth-century examples (see Tables 1a and 1b). One of these is seen in the red cloak of the servant in Giovanni Antonio Pellegrini's *Rebecca at the Well* (NG 6332),

painted 1708–13 (PLATE 5). The strong broad band at  $c.3400\text{--}3300\text{ cm}^{-1}$  and the series of strong bands at 1154, 1083, 1048 and 1023  $\text{cm}^{-1}$  seen in the IR spectra of these inclusions are typical of starch and in the majority of cases they show a characteristic cross shape under cross polars (PLATE 6).<sup>48</sup> Starch was also mixed with the majority of the examples of nineteenth-century cochineal-based pigments examined (see Table 1b). All those analysed were on tin-containing substrates (sometimes also containing minor amounts of aluminium and/or calcium) and consisted of small, strongly coloured cherry-red particles. An example from Pierre-Auguste Renoir's *A Nymph by a Stream* (NG 5982) of 1869–70 (PLATE 7) is seen in PLATES 8a and 8b; the FTIR spectrum is shown in FIG. 1.

In one pigment, used for a deep red flower in *The Painter's Garden at Saint-Privé* (NG 1358) painted by Henri-Joseph Harpignies in 1886, a different extender is present. Here the cochineal pigment, which appears from IR analysis to be a carmine, is mixed with colourless particles of chalk. Chalk was also found associated with the cochineal pigment in Monet's *Lavacourt under Snow* (NG 3262), painted about 1878–81. The unusual large rounded particle form suggests that the chalk was artificially precipitated and dyestuff can be seen clinging to the colourless particles.

### Madder

In about 1771, the German chemist Andreas Sigismund Marggraf was given a small sample of red pigment. The method of manufacture had been lost with the death of its maker and Marggraf was, in effect, asked to rediscover it. He was able to determine that the pigment consisted of a red colouring matter on an alumina substrate; in other words, it was some kind of lake pigment. After failing to make a successful match using the dyes extracted from cochineal, kermes, sticklac, Polish cochineal and various redwoods, he finally succeeded using the colouring matter extracted from the best *Färberröthe* (madder root) in a hot solution of Roman alum (potassium aluminium sulphate), precipitating the lake pigment with a solution of salt of tartar (essentially potassium carbonate).<sup>49</sup> Later writers gave Marggraf the credit of being the first to prepare, or to have rediscovered, a red lake pigment from madder, while recognising that the colour was already known by the Greeks and Romans and that the Florentine Antonio Neri had described a method for making a madder lake in 1612.<sup>50</sup> In fact, madder lakes had been widely used in Europe in the fifteenth, sixteenth and seventeenth centuries, but the method of making them from cloth

shearing had perhaps disguised this from later commentators.<sup>51</sup>

As we have seen, Marggraf's work coincided with a greatly increased demand for madder across Europe, stimulated by the desire to reproduce the brilliant red colour, Turkey red or *rouge d'Andrinople*, seen on imported cottons and obtained with madder by a complex and time-consuming method. Knowledge of the method was eventually obtained by industrial espionage in Greece and Turkey where dyeing was carried out and, and in the case of France, craftsmen from Smyrna (now Izmir), Salonica and Andrinople (or Adrianople, now Edirne) were persuaded to come and work in French factories.

Madder cultivation and processing had been an important industry in the Netherlands for several centuries and a valuable export commodity; now it was encouraged across Europe, notably in France and Germany. In England, one of those interested in the cultivation of madder was George Field, already famed for his madder lake pigments by the early nineteenth century. Field was awarded a silver medal by the Society of Arts in London for a madder-drying stove in 1806 and two years later had built a factory for the large-scale production of lakes at Conham near Bristol. Later he invented a form of percolator for preparing lakes for which he was also honoured with a medal.<sup>52</sup> The interest in madder colours was not confined to Field: in 1804 Sir Henry Englefield was awarded a Society of Arts silver medal for his madder lake, prepared from washed madder root by extracting the dyestuff into cold water under pressure, then heating the coloured liquid, adding alum and precipitating the lake with potassium or sodium carbonate.<sup>53</sup> Field's notes on madder lakes ('Rubic lakes') appear in a book entitled *Rubia. Experiments on madder 1804* and are scattered in several of his other notebooks. He tried various methods for extracting the dyestuff and also tried different metal salts to form the substrate, such as copper and iron sulphates.<sup>54</sup> The colours obtained were browns and purples. Pigments with names such as Brown Madder and Purple Madder appear in colour merchants' catalogues certainly from the 1840s, but it is hard to know if these were always made with madder dye and an iron or copper salt; sometimes these colours were prepared by mixing other pigments.<sup>55</sup>

By the end of the century, the French madder industry, centred principally in the regions of Alsace and around Avignon, had grown to the point where it overtook that of the Netherlands; England, with its thriving calico printing and Turkey red dyeing industries, was a major consumer. French and Dutch



PLATE 7 Pierre-Auguste Renoir, *A Nymph by a Stream* (NG 5982), 1869–70. Canvas, 66.7 × 122.9 cm.

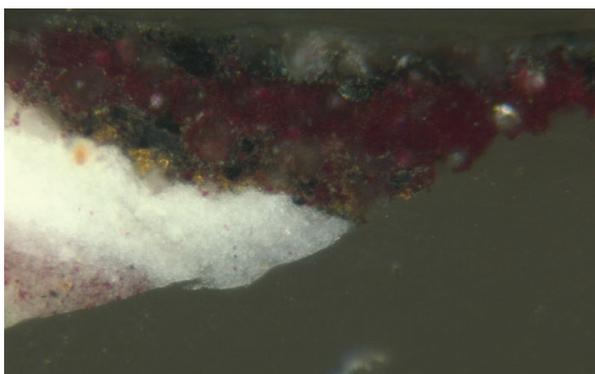


PLATE 8a Pierre-Auguste Renoir, *A Nymph by a Stream* (NG 5982). Cross-section of a sample from brownish-red paint in the background. The uppermost layer consists of cochineal carmine extended with starch. Original magnification 400×, actual magnification 350×.

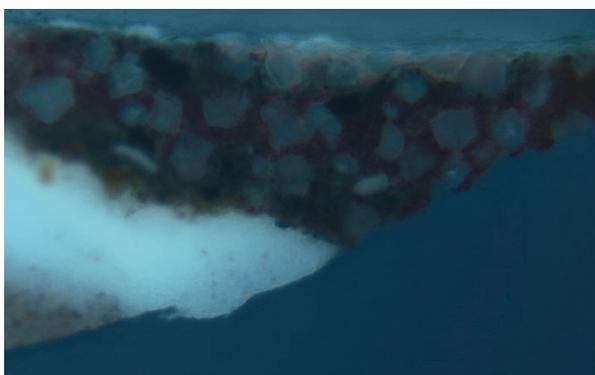


PLATE 8b Cross-section shown in PLATE 8a under UV illumination; the rounded starch particles with a bluish-white fluorescence are clearly visible in the red lake layer. Original magnification 400×, actual magnification 350×.

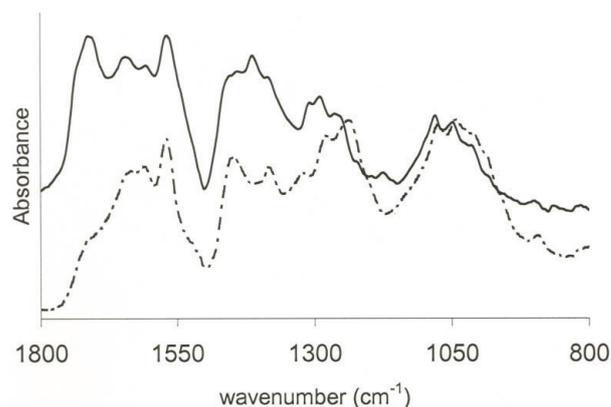


FIG. 1 Infrared spectrum (1800–800  $\text{cm}^{-1}$ ) of: (i, solid line) Renoir, *A Nymph by a Stream* (NG 5982), cochineal carmine from the sample illustrated in PLATE 8a; (ii, dotted line) Sn-containing carmine produced in the laboratory based on Leuchs 1829, Vol. 2, p. 145 (see Table 2 and PLATE 2c). A strong band around 1570, bands at  $c.1450$  and  $1383$ , features around 1300–1250 and the doublet at  $c.1083/1045$   $\text{cm}^{-1}$  are typical of Sn-containing carmine pigments (Al-containing carmines are similar). The binding medium bands ( $c.1730$  and  $1412$   $\text{cm}^{-1}$ ) mask the absence of bands associated with the carboxylic acid function, one of the features which distinguish carmine pigments from carminic acid.

madder suppliers competed to supply the huge demand for madder or its derivatives until the 1870s, when the consequences of the successful synthesis of the most important constituent of the dye, alizarin, inevitably began to have an effect on trade.<sup>56</sup>

The conditions under which madder is grown affect the quality of the dye. In France the chalky, humus-rich soils of the *paluds* of the Vaucluse encouraged the formation of madder roots which gave bright red dyes; the Levant madders, which were thought to be the best, were also of this type. Roots from madders grown in clay-rich soils with little lime, including the Alsace madders, tended to give more orange colours. Calcium salts were often added to the dye bath to counteract this. In practice, good madders had similar tinctorial powers; these depended on the climate in which the roots were grown, the length of time they had been in the soil, variations in atmospheric conditions during drying, and care in grinding and storage.

As had long been the case with Dutch madders, the Avignon and Alsace madders were graded according to the size and degree of processing of the root. Thus an Alsace madder graded SF – *surfine* or super fine – was equivalent to the best Dutch grade, *krap*, and consisted of large roots, with the outer epidermal layers and small rootlets removed; the medium fine, MF, grade consisted of these small rootlets and other small roots (the Dutch *gemeen* grade), and so on. Avignon grades were similar, but also took account of whether the roots were from madder grown on the *paluds* (P). For the best lake pigments the highest grade of madder was needed: extra superfine madder from the *paluds* in Avignon or super-superfine in Alsace, taken from the heart of the large roots.<sup>57</sup>

Much of the madder produced was processed to give derivatives that were a richer source of dye and thus more economical in use; this counterbalanced their higher cost. Following the isolation of alizarin (1, 2-dihydroxyanthraquinone), the principal constituent of the madder dye, and purpurin (1, 2, 4-trihydroxyanthraquinone) by Pierre-Jean Robiquet and Jean-Jacques Colin in 1826,<sup>58</sup> various methods of treating the root by fermentation or extracting it with more or less concentrated acid (usually sulphuric) were introduced. The aim was to obtain alizarin, which is present in the root largely in the form of a glycoside, ruberythric acid, in a free state for all the colouring purposes for which madder was used, including lake making.<sup>59</sup> It is suggested by Robert Mallet in his 1870 revision of George Field's *Rudiments of the Painter's Art* (London 1850), itself taken from the earlier *Chromatography* (London 1835),

that madder colours had been derived from 'pure alizarine' for many years.<sup>60</sup> The limited analysis that has been carried out suggests that this is not accurate; also the alizarin must have been the natural form at that date. Little free purpurin is present in the root at all; most is produced by decarboxylation of pseudopurpurin, purpurin-3-carboxylic acid (1, 2, 4-trihydroxyanthraquinone-3-carboxylic acid), itself present in the root as the glycoside galiosin. Both acid treatment and fermentation encourage breakdown of these sugar-containing precursors, liberating the free anthraquinones. The most important of these dye-enriched madder derivatives was garancine, patented by Colin, Robiquet and colleagues on 26 March 1828, which was made by treating the washed, powdered root with sulphuric acid, followed by washing, steam-heating to boiling, further washing and, finally, drying the product.<sup>61</sup> This was used for lake making by boiling it with twice its weight of alum in pure water, filtering it and adding sufficient sodium carbonate solution to the warm filtrate to precipitate the lake. Writing in 1855, Jules Lefort was of the opinion that most of the lakes used for painting in France were made from garancine.<sup>62</sup> Other similar, sometimes weaker, products included flowers of madder and *garanceux*. In most of these processes, the large amounts of waste liquid could be fermented to give alcohol.

One early to mid-nineteenth-century method to prepare lake pigments, devised by a M. Colomb or Collomb, consisted of macerating the madder in dilute nitric acid, washing it and treating it with caustic soda solution to give a violet alkaline solution. Addition of nitric acid gave a voluminous precipitate which was washed and treated with boiling alum solution. Neutralisation with sodium carbonate gave the lake pigment on a hydrated alumina substrate, or addition of further acid gave the dyestuff.<sup>63</sup>

A different approach involved extraction of the water-soluble glycosides from the raw root. In the best-known method, devised by Emile Kopp, madder was soaked with water saturated with sulphurous acid (H<sub>2</sub>SO<sub>3</sub>); a little concentrated sulphuric acid was then added to the filtrate and the temperature raised to about 50–60 °C, when brownish flakes of a mixture of pseudopurpurin, purpurin and traces of other anthraquinones precipitated. This material, known as Kopp's purpurin, was widely used in France for lake pigments until the early twentieth century. Heating the liquor further caused the precipitation of a green alizarin-containing mixture.<sup>64</sup>

Some French madder pigments were extremely expensive. Ordinary commercial lakes were 30 francs a

pound (the French pound contained 16 ounces); the high-quality pigments made by Charles Bourgeois, M. Cossard and J.F.L. Mérimée were expensive, Bourgeois's and Cossard's pigments costing 15 francs an ounce.<sup>65</sup> Around 1828 Colin and Robiquet devised a method of making lakes by macerating madder in water and submitting it to pressure before heating it with alum solution, filtering it and precipitating the lake by the addition of sodium bicarbonate.<sup>66</sup> These pigments could be made in a few hours and, during a trial made by Michel-Eugène Chevreul and Louis-Jacques Thénard for the Paris Académie Royale des Sciences, were found to compare favourably in colour and covering power. Furthermore, Colin and Robiquet thought that their lakes could be sold at 20 francs a pound – clearly a considerable saving. Bourgeois's pigment, which appeared in 1816, was known as *carmin de garance*, madder carmine, and it was described by Chevreul and Thénard as having a pronounced violet tone by comparison with the other pigments tested. His method of preparation was kept secret, but a similar product could be made from the best madder, fermented and treated with diluted sulphuric acid. This was left to stand, diluted and filtered through powdered glass into a vessel of pure water. The colour, essentially pure madder dyestuff and not a lake, settled out;<sup>67</sup> it was given the name *carmin de garance* by analogy with cochineal carmine. *Carmin de garance* was one of the most expensive pigments in French colourmen's catalogues, but it was not always pure madder; sometimes it also contained cochineal dyestuff. Lake paints containing both cochineal and madder dyes were found in several of the paintings listed in Table 1b, including Seurat's *Bathers at Asnières* (NG 3908) of 1884–6, but it is not possible to be sure if this is a manufacturer's mixture or if the artist mixed it himself on the palette.<sup>68</sup>

This discussion has concentrated on French madder pigments because the nineteenth-century French School is well represented in the National Gallery Collection and, in those cases where examination of red lake pigments used has been possible, madder lakes have frequently been identified, as can be seen from Table 1b. Also, madder lakes formed a significant part of the range of pigments available to the French painter, particularly in the middle decades of the century. A wholesale catalogue of Lefranc et Cie from 1858, updated in 1867, lists over thirty lake pigments that were probably derived from madder: nine or ten *laques de garance cristallisées*, eight *laques de Robert*, eight *laques de Rome* (the identity of which is not certain) and fifteen *laques de Smyrne*, as well as *carmin de garance*,<sup>69</sup> and while this number was reduced

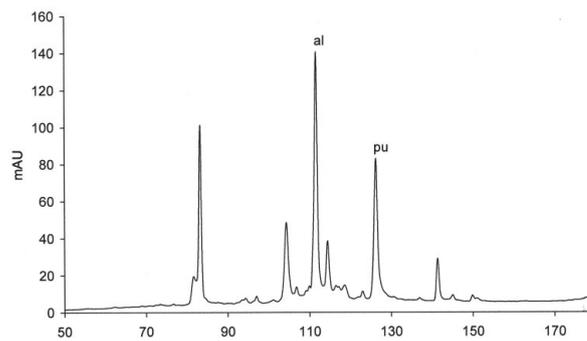


FIG. 2a HPLC chromatogram of an aqueous extract of garancine (Leeds Collection, Department of Colour Chemistry, Leeds University), evaporated to dryness, after overnight treatment with 4% boron trifluoride/ methanol: al 31%, pu 21%, others 48%. (The large constituent at 83 mins eluting slightly later than ruberythric acid – absent here – is an unidentified anthraquinone.)

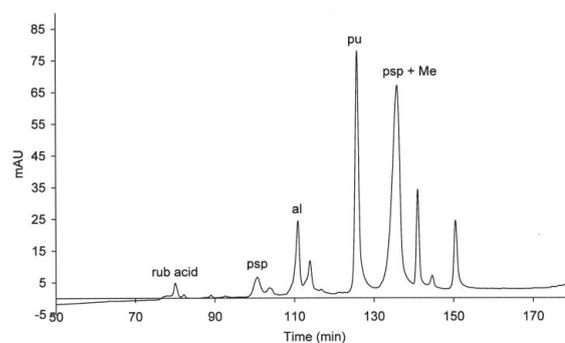


FIG. 2b Chromatogram of pigment made during a workshop held at the Instituut Collectie Nederland, Amsterdam, April 2004, using a sample of 'Kopp's purpurin' prepared in the National Gallery laboratory, dyestuff extracted with 4% boron trifluoride/ methanol: rub acid 1%, al 6.5%, pu 26%, total psp 50%, others 16.5%.

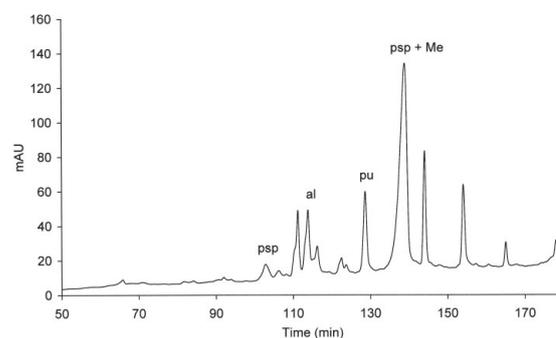


FIG. 2c Attributed to Pierre Andrieu, *Still Life with Fruit and Flowers* (NG 6349): sample of madder lake used for dark red glaze, dyestuff extracted with 4% boron trifluoride/ methanol: al 10%, pu 9%, total psp 51%, others 30%. Key: rub acid: ruberythric acid; psp: pseudopurpurin; al: alizarin; pu: purpurin; psp + Me: methylated pseudopurpurin; other constituents and methylated derivatives unidentified. Chromatograms recorded at 254 nm; detail of region recorded between 50–180 min shown.



PLATE 9 Attributed to Pierre Andrieu, *Still Life with Fruit and Flowers* (NG 6349), probably c.1850–64. Canvas, 65.8 × 81 cm.

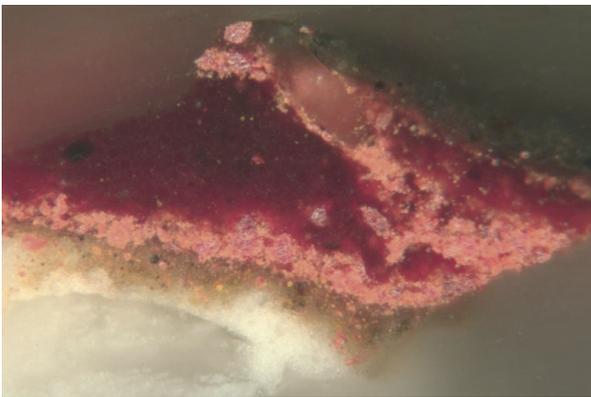


PLATE 10 Attributed to Pierre Andrieu, *Still Life with Fruit and Flowers* (NG 6349). Cross-section of dark-red glazy paint from middle of top edge; the uppermost red paint layer contains red lake with a high phosphorus content, a little bone black, vermilion and siliceous iron earth pigment. Original magnification 400×, actual magnification 350×.

considerably later in the century, madder remained important for the preparation of artists' pigments, even after synthetic alizarin had swept the board for other purposes.

The different methods of treating the madder to extract the colouring matter can result in a variation in the number and identity of dyestuff constituents present. The principal differences are that if madder root treated with acid to hydrolyse the glycosides – garancine or a similar product – was used in the preparation of the pigment, little of the glycosides, such as ruberythric acid (alizarin-2- $\beta$ -O-primeveroside), will be present; pseudopurpurin, which is converted to purpurin, will also be largely absent. FIG. 2a shows the chromatogram from a nineteenth-century sample of garancine (Department of Colour

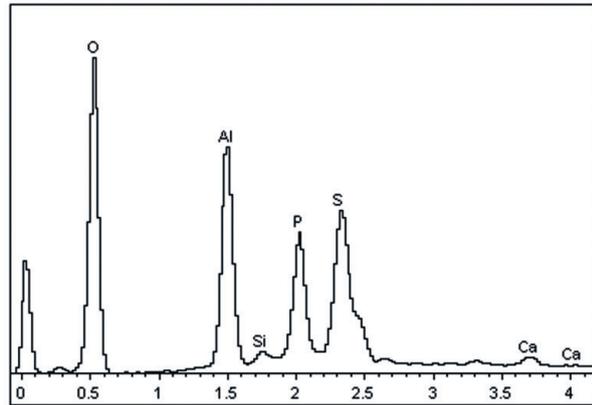


FIG. 3 EDX spectrum from a red lake particle in the sample shown in PLATE 10. As well as Al and S (sulphate), the spectrum shows a phosphorus (phosphate) peak far larger than that expected from the dyestuff; a phosphate salt is likely to have been used in the manufacture.

Chemistry, Leeds University), treated with 4% boron trifluoride/methanol in the same way as that used to derivatise paint samples for analysis; this contains high proportions of free alizarin and purpurin, without their glycosides and no pseudopurpurin.<sup>70</sup> If, however, a product such as Kopp's purpurin was used as the source of dye, much of the pseudopurpurin survives the mild acid treatment and is present in the final pigment, whereas the alizarin content is very low: alizarin remains in solution at the temperature at which pseudopurpurin precipitates, as described above. In the example illustrated in FIG. 2b, a lake made during a workshop held at the Instituut Collectie Nederland, Amsterdam, in 2004, the pseudopurpurin used was prepared in the National Gallery laboratory following the original recipe for Kopp's purpurin; a little alizarin did precipitate in this case.<sup>71</sup> The madder lake used in the *Still Life with Fruit and Flowers* (NG 6349), attributed to Pierre Andrieu and probably dated about 1850–64 (PLATES 9 and 10), shows a high pseudopurpurin content and is clearly not derived from garancine; it may be a little early in date for Kopp's purpurin to have been used, however (FIG. 2c).<sup>72</sup>

In several of the later paintings examined, including Edgar Degas's *Portrait of Elena Carafa* (NG 4167) of about 1875, and Claude Monet's *Flood Waters* (NG 6278) of about 1896, *The Water-Lily Pond* (NG 4240) of 1899 and *Irises* (NG 6383) of 1914–17, the pigments were found to have a very low alizarin content indeed and a very high pseudopurpurin content (around 90% in the case of the two later Monets); here Kopp's purpurin is likely to have been used. These pigments are a brilliant, transparent

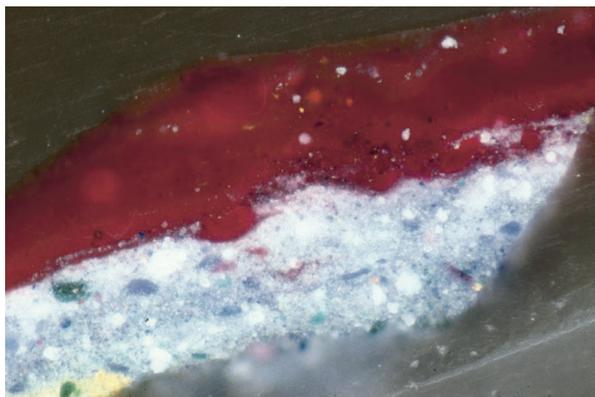


PLATE 11 Claude-Oscar Monet, *Irises* (NG 6383), c.1914–17 (see p. 61). Cross-section of a deep purplish stroke of paint; the uppermost layer contains madder lake. Original magnification 240 $\times$ , actual magnification 210 $\times$ .

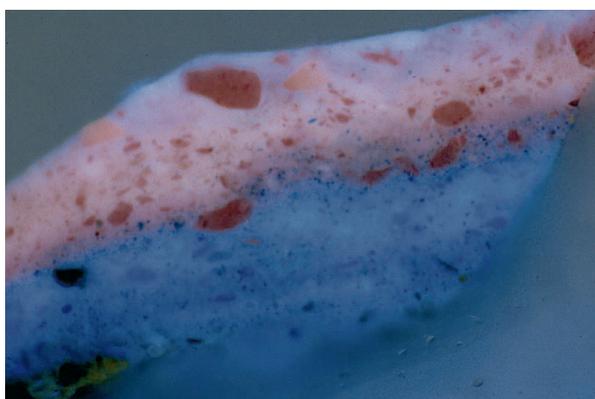


PLATE 12 Cross-section shown in PLATE 11 under UV illumination, showing the strong pinkish-orange fluorescence of the madder lake. Original magnification 240 $\times$ , actual magnification 210 $\times$ .

orange-red in oil medium with a marked orange fluorescence under UV illumination (PLATES 11 and 12).<sup>73</sup> Similar findings have been reported in the paintings of Van Gogh, Redon and Renoir.<sup>74</sup>

A characteristic feature of Kopp's purpurin itself is the presence of sulphur, detectable by EDX analysis. Sulphur can also be present in substantial amounts in the lake pigment as a result of the method used to prepare the pigment substrate. As discussed above, preparation of the lake substrate by the addition of alkali to alum, as had become common practice by the late eighteenth century, results in the incorporation of sulphate ions brought down during the precipitation. Secondly, in a method devised by Jean-François Persoz, madder pre-soaked in sodium sulphate, then rinsed, was boiled for 20 minutes in a 10% solution of alum, filtered hot and allowed to cool to about 40°C before only two-thirds of the calculated amount of alkali (commonly sodium carbonate)

was added and the mixture was boiled to precipitate the lake. The substrate formed was described as a basic aluminium sulphate and had the considerable advantage that it was not gelatinous and was easy to filter and wash. Lead acetate could be used as a precipitating agent instead of sodium carbonate.<sup>75</sup>

A high sulphate content is seen in all the madder lakes identified in Table 1b and it is likely that one or other of these methods was used to prepare them, probably the latter. In terms of the substrate composition, the madder lake in the deep purplish paint used by Monet in his *Irises* (NG 6383) of about 1914–17 is very similar to the madder lakes he used earlier in his career and is a typical example. The pigment shows large peaks for Al and S (same peak height as Al) in the EDX spectrum. The sulphate content can be detected by FTIR spectroscopy (bands characteristic of S–O vibrations at 1125 and 985  $\text{cm}^{-1}$ ) and the substrate is closely similar to the light alumina hydrate described in paint technology literature. The substrate of the lake used by Renoir in his painting of 1876–7, *La Première Sortie* (NG 3859), is of this type, but in this case the IR spectra are dominated by two sharp bands at c.1582 and 1465  $\text{cm}^{-1}$ .<sup>76</sup> These were seen, to a greater or lesser extent, in all the madder lakes examined and in many of the cochineal pigments; they have sometimes been noted in association with lake pigments of earlier date. Experiments with test plates aged under conditions of high relative humidity have shown that bands appear at the same positions when various types of aluminium-based substrates,<sup>77</sup> prepared in the absence of dyestuff, are painted out in cold-pressed linseed oil. These experiments suggest that the bands may correspond to aluminium soaps formed by reaction between the aluminium in the lake substrate and the oil medium.<sup>78</sup> The high proportion of oil and addition of driers often used with red lake pigments may promote this reaction; many of the samples studied contained significant quantities of lead soaps. It should, however, be borne in mind that late in the nineteenth century aluminium stearate was added to tube paints to help prevent settling.<sup>79</sup>

The dark red glazy paint from Andrieu's painting discussed above has a slightly different substrate. Here the madder lake contains Al and S, but also a large quantity of phosphorus (FIG. 3). Although low levels of P may be associated with the dyestuff source,<sup>80</sup> the proportion of phosphorus in this lake suggests the use of (sodium) phosphate as the precipitating agent during lake manufacture. The slight shift in the position of the sulphate band in the IR spectrum to lower wavelength (c.1100  $\text{cm}^{-1}$ ) is consistent with the high phosphate content.

### Other colouring matters

The evidence from this survey of the lake pigments used in eighteenth- and nineteenth-century paintings in the National Gallery Collection supports the information provided by contemporary pigment recipes and other sources: artists' pigments were predominantly based on cochineal and madder dyestuffs. Other dyestuffs used in earlier periods for pigment preparation, such as kermes, brazilwood, *Caesalpinia* spp., and lac dye, produced by the Indian lac insect *Kerria lacca* (Kerr) and other species, were still in use, brazilwood quite widely, but those from lac and kermes seem only to have had a limited application.

The dyestuff brazilein extracted from the so-called 'soluble' redwoods, known colloquially as brazilwood, was not lightfast, but it was widely used during the period under discussion for ephemeral or commercial applications where permanence was unimportant, and for cheap pigments. Lake pigments were prepared in a variety of ways: by mixing the dyestuff with alum solution and precipitating it with alkali, or the same tin salts as those used with cochineal, or both; by adding a mixture of starch, chalk and gypsum to a decoction of brazilwood and then adding alum and leaving the mixture to stand, adding more brazilwood extract and alum until the desired colour was obtained; or simply by adding chalk to a solution of the dyestuff containing alum. These pigments often went under the names of *Kugellack*, Viennese lake and even Florentine lake and other names formerly associated only with cochineal and, earlier, kermes.<sup>81</sup> The tin-containing pigment appears to have been common, in France at least. Brazilwood dyestuff was also used to falsify madder lakes particularly, or was added deliberately (as dyestuff or in lake form) to make a cheaper grade of pigment.<sup>82</sup> It has been identified in lake pigments used by Vincent van Gogh, including a tin-containing lake extended with starch, a composition very similar to the tin-containing cochineal pigments found in several National Gallery paintings. This pigment, which would have been a bright crimson when purchased, has faded particularly badly. In other examples, the brazilwood pigment was associated with a purpurin- or pseudopurpurin-containing pigment in circumstances which suggest that the artist mixed the lakes himself, and in one case it was present with a different madder pigment: here the mixture of pigments may have been made at some stage during the manufacture of the tube paint. In every case, the brazilwood component had faded, with sad consequences for the appearance of the paintings.<sup>83</sup>

The lac insect was the source of shellac, used in varnishes, as well as the lac dye and both sticklac (the

crude material as broken from the host trees) and shellac continued to be imported into England from India during the eighteenth century. However, it is very unclear to what extent the dye was employed before its use was encouraged by Edward Bancroft as if it were a new unknown dyestuff, which was far from being the case as far as lake pigments were concerned.<sup>84</sup> By the nineteenth century the crude dyestuff extracted during purification of the shellac was exported from India in cake form.<sup>85</sup> It was used for dyeing to some extent in eighteenth- and nineteenth-century Europe to replace, or in addition to, cochineal. This use may have been greater in the United Kingdom; it was regularly used by Scottish tartan manufacturers in the early part of the century, although to a lesser extent than cochineal.<sup>86</sup> Its use as a pigment at this time is harder to assess, but the pigment referred to in contemporary English artists' manuals as Indian lake may well have contained lac dyestuff. George Field examined some samples of Indian lake, described as lac lakes, and Indian Lake was listed in Winsor & Newton's catalogues throughout the second half of the nineteenth century at a price similar to, or a little less than, the cochineal-based crimson lake.<sup>87</sup> However, there is no mention of the pigment under this name in, for example, Lefranc catalogues of the same date.<sup>88</sup>

After the arrival of New World cochineal, the use of kermes for dyeing decreased greatly in Europe so that it was only carried out in a very few centres, including Genoa and Venice (Italy), Orleans (France) and Vienna (Austria).<sup>89</sup> Kermes lake pigments were available to a limited extent, at least until the earlier nineteenth century, in France and Italy. Kermes lake was identified in the pigment used for the restoration of the red dress of the Virgin Mary in Boltraffio's *Virgin and Child* (NG 728), painted in Milan in 1493–9; the dress, together with other areas of the painting, was repainted in a medium containing mastic varnish probably before 1854, when the painting left Italy.<sup>90</sup> George Field tested the permanence of kermes lakes 'in very small drops of a powdery texture – crimson tone – works well – moderately powerful' obtained in Paris and wondered if indeed they contained kermes dye as they seemed less affected by his tests than the crimson cochineal lakes he examined.<sup>91</sup>

As the nineteenth century progressed, developments in the understanding of the chemistry of organic substances were linked with the production of an ever-increasing number of synthetic dyes in a wide range of colours, many unobtainable (indeed, unimaginable) before. Vivid, gaudy and very variable in

permanence, they were tried for dyeing, the graphic arts, interior decoration, and all the purposes for which natural dyes had once been the only source of colour. Some found their way onto the painter's palette, but poor lightfastness dictated that most of these had a short life as artists' colours.<sup>92</sup> A very few were sufficiently reliable and remained in use well into the twentieth century. The most important were derived from the synthetic form of alizarin, the principal constituent of the madder dye. The successful synthesis of alizarin was patented by Carl Graebe and Carl Liebermann in 1868 and synthesis on a commercial scale was begun by Heinrich Caro, of the Badische Anilin- und Soda-Fabrik (BASF), in 1869. It is not surprising that in France, where 21,000 hectares were used for madder cultivation in 1862, much of the resistance to synthetic dyes like the new alizarin came from the agricultural sector: this area was halved by 1878 and in 1881 it was estimated that dyeing with synthetic alizarin was three times cheaper than with natural madder. In practice madder and its synthetic counterpart co-existed fairly amicably until the end of the nineteenth century, partly because the stability of alizarin was thought uncertain, partly because, although alizarin increasingly came to be used for dyeing cotton, madder remained important for dyeing wool.<sup>93</sup> By the end of the century, a variety of recipes were available for preparing pigments from synthetic alizarin, synthetic purpurin and related dyes; it was also recognised that alizarin lakes were the most permanent of all those made from the artificial dyes then available. However, they were also the most difficult to make: a calcium salt was necessary, together with the aluminium salts and sodium carbonate, to ensure brilliance and fastness of colour; the use of oleic acid or Turkey-red oil also helped in this respect; it was essential to exclude iron, or else the pigment became brown; and it was important to control the time taken for the procedures, as the colour was affected by carrying out processes too quickly (PLATE 13).<sup>94</sup> By the 1890s, Winsor & Newton included alizarin lakes among their products.<sup>95</sup> One of the paintings examined for this survey was found to contain alizarin crimson: *Torchlight Procession* (NG 5009), ascribed to Adolphe Monticelli, but probably painted by an imitator of his work. The pigment has a calcium carbonate extender and is unlike all the lakes identified in genuine Monticelli paintings, which contain cochineal dyestuff and starch extenders. It is thought that the picture could have been painted between 1870 and 1886; in fact, it must date from the end of this date range and it could have been painted very much later.

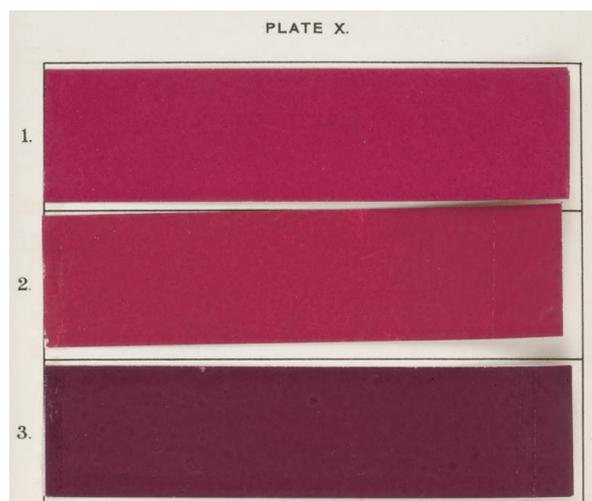


PLATE 13 Examples of alizarin lakes from F.H. Jennison, *The Manufacture of Lake Pigments from Artificial Colours*, London 1900, plate 10, facing p. 95 (from top): 1) aluminium lake of alizarin made very slowly; 2) same as no. 1, made quickly; 3) same as no. 1, but contaminated with iron.

It is important to remember that artists' paints are only one of the many applications to which pigments could be put and the range of other, less permanent, synthetic colouring matters – triphenylmethane derivatives such as magenta (fuchsine, rosaniline hydrochloride), methyl violet (tetra, penta, and hexamethylparosaniline) and Brilliant green (a form of malachite green), or other varieties such as eosin (the potassium salt of tetrabromofluorescein and related compounds) – could also be used for wallpapers, stained papers, printing inks, posters and all kinds of other, relatively ephemeral uses.<sup>96</sup> Eosin, aniline purple or mauveine and methyl violet are among those that were used to make artists' pigments and four *laques d'aniline* – *laque géranium*, *pourpre d'aniline*, *violet magenta* and *violet solférino* – appear in the 1890 Lefranc catalogue, all at a price rather less than the equivalent-sized tubes of carmine and the madder lakes.<sup>97</sup> None of these dyestuffs has so far been identified in paintings in the National Gallery, but it is well known that Vincent van Gogh used a fugitive *laque géranium* containing eosin in a number of paintings.<sup>98</sup>

### Conclusions

Substantial changes took place in the manufacture of red lake pigments from around the end of the eighteenth century. The increasingly rapid progress made in all aspects of the dyeing and pigment manufacturing industries is reflected in the very different results seen during analysis of the pigments of these years compared with those from earlier times. The information given by literature of the period helps towards an

understanding and interpretation of sometimes very complex results. There is a limit to the extent to which a distinction can be made between lakes containing the same basic ingredients, but made to different recipes, although some tentative conclusions can be drawn. It is, for example, very difficult to decide where on the carmine–cochineal lake continuum a particular example may fall and, in nineteenth-century examples particularly, this may be complicated by the extenders added by the paint manufacturer or colourman at some stage in making the tube paint. In the same way, most of the madders contained some sulphate in the substrate, but several different methods of making the pigment can be responsible for this. In addition, the many different ways of processing madder to obtain the dye may give different results, both qualitatively and quantitatively, by HPLC analysis, but the survey was too limited to give a sense of this.

While it cannot be considered comprehensive, the survey of red lake pigments in National Gallery paintings is extensive enough to reflect what was on the market, in spite of the fact that it necessarily concentrates on paintings from particular geographical areas because of the nature of the National Gallery Collection. Having said that, it is important to note that had the survey looked at a selection of eighteenth-century German and nineteenth-century English paintings, the results and pigment characteristics observed might be very different. A recent study indicates, for example, that tin-containing cochineal pigments were already available in Germany in the second half of the eighteenth century.<sup>99</sup>

Two points have become clear from the study. First, little change appears to have taken place in the methods of making the cochineal-containing pigments after the turn of the nineteenth century: the recipes then available recur again and again for the next one hundred years and into the twentieth century. Secondly, the painters studied appear to have had an affection for a very particular type of madder pigment, one that gave a vibrancy and brilliance of colour that would have been particularly important in the palette of painters like Monet and Renoir. It is interesting that an impression of a wide range of choice of both cochineal and madder pigments is given by French colourmen's catalogues in the mid-nineteenth century, which appears to decrease later. However, some of these pigments may have been intended for uses other than fine arts, so may have been of insufficient quality and permanence to be used for such purposes.

It is somewhat ironic that the study and quest for

efficiency in the processing of madder, which led to the isolation and identification of alizarin, its principal constituent, finally contributed to the downfall of the very industry that spawned it. The elucidation of alizarin's chemical structure was followed by its synthesis, and thus the growth of a new, large and successful chemical industry, not in France, where so much of the early analysis and research had been carried out, but in Germany. Painters, however, retained an affection and desire for the subtlety and complexity of colour given by the true madder pigments and not obtainable from alizarin, which has endured to this day.

### Acknowledgements

The paintings in this study were examined during conservation treatment or routine cataloguing of the eighteenth- and nineteenth-century Schools. We would like to thank Ashok Roy, Rachel Grout and Emily Gore for their valuable contribution to this survey, and Mark Richter (Technische Universität, Munich) and Mark Clarke (Hamilton Kerr Institute, Cambridge) for useful discussions. We are grateful to Winsor & Newton, the Rijksbureau voor Kunsthistorische Documentatie (RKD) and the De Mayerne Programme for access to their Nineteenth-Century Archive project database.

### Notes

- 1 *Natural Dyestuffs and Industrial Culture in Europe*, ed. R. Fox and A. Nieto-Galan, Canton MA, 1999, pp. ix–xxix; A.S. Travis, 'Between Broken Root and Artificial Alizarin: Textile Arts and Manufactures of Madder', *History and Technology*, 12, 1994, pp. 1–22, esp. pp. 1–5; E. Homburg, 'The Influence of Demand on the Emergence of the Dye Industry. The Roles of Chemists and Colourists', *Journal of the Society of Dyers and Colourists*, 99, 1983, pp. 325–32, esp. pp. 326–9.
- 2 J. Hudson, *The History of Chemistry*, Basingstoke and London 1992, pp. 244–54.
- 3 A. Nieto-Galan, *Colouring Textiles: A History of Natural Dyestuffs in Industrial Europe*, Dordrecht 2001, pp. 19–21; Travis 1994 (cited in note 1); P. Schützenberger, *Traité des matières colorantes comprenant leurs applications à la teinture et à l'impression et des notices sur les fibres textiles, les épaississants et les mordants*, 2 vols, Paris 1867, Vol. 2, pp. 68–83.
- 4 D. Cardon, *Le monde des teintures naturelles*, Paris 2003, pp. 484–5, 492; R.A. Donkin, 'Spanish Red: an Ethnogeographical Study of Cochineal and the *Opuntia Cactus*', *Transactions of the American Philosophical Society*, N.S., 67, 5, 1977, pp. 1–84; C. Rahn Phillips, 'The growth and composition of trade in the Iberian empires, 1450–1750', in *The Rise of Merchant Empires: Long-Distance Trade in the Early Modern World, 1350–1750*, ed. J.D. Tracy, Cambridge 1990 (1993 reprint), pp. 34–101.
- 5 Hudson (cited in note 2), pp. 247–8.
- 6 J. Kirby, M. Spring and C. Higgitt, 'The Technology of Red Lake Pigment Manufacture: Study of the Dyestuff Substrate', *National Gallery Technical Bulletin*, 26, 2005, pp. 71–85, esp. pp. 80–1; T. Sato and K. Sato, 'Preparation of Gelatinous Aluminium Hydroxide from Aqueous Solutions of Aluminium Salts Containing Sulphate Group with Alkali', *Journal of the Ceramic Society of Japan, International Edition*, 104, 1996, pp. 359–63; light alumina hydrate, approximate formula  $\text{Al}_2\text{O}_3 \cdot 0.3\text{SO}_3 \cdot 3\text{H}_2\text{O}$ : T.C. Patton, 'Light Alumina Hydrate and Gloss White', in *Pigment Handbook*, ed. T.C. Patton, New York 1973, Vol. 1, pp. 319–21.
- 7 L. Molà, *The Silk Industry of Renaissance Venice*, Baltimore and London 2000, pp. 120–31.
- 8 Rahn Phillips 1990 (cited in note 4), pp. 79–81; see also the discussion of

- shipping and trade by way of the Spanish Indies in this chapter. For cultivation of and trade in the insect see Donkin 1977 and Cardon 2003, pp. 484–6, 492 (both cited in note 4).
- 9 Kirby, Spring and Higgitt 2005 (cited in note 6), p. 78.
  - 10 A. Neri, *L'arte vetraria distinta in libri sette del R.P. Antonio Neri, fiorentino ...*, Florence 1612, pp. 99–103. Neri himself does not mention *grana* (kermes) at all and comments that to make a lake from *verzino* (brazilwood) or *robbia* (madder) more will be needed than when using *chermisi*, as this is richer in colour than either of the plant sources. In the English edition of the book, Christopher Merret translated *chermisi* as cochineal, which he distinguishes clearly from kermes (spelled Chermes!) in his descriptive notes: see *The Art of Glass, wherein are shown the wayes to make and colour glass, pastes, enamels, lakes ...* [trans. C. M.], London 1662, pp. 172–80, 346–9. In the later French translation from the German edition of Johann Kunckel, the insect is translated as *kermès*: see *Art de la verrerie de Neri, Merret et Kunckel ...*, trans. from the German edn by M. D.\*\*\* [i.e. Paul Thiry, Baron d' Holbach], Paris 1752, pp. 241–52. For Neri himself see L. Zecchin, *Vetro e vetrai di Murano: Studi sulla storia del vetro*, Vol. 1, Venice 1987, pp. 85–91, first published as 'Sulla storia delle conterie veneziane: tecnologia in versi', *Giornale Economico della Camera di Commercio* (Venice), VIII, 1954, pp. 80–5.
  - 11 T. Ishida, M. Inoue, K. Baba, M. Kozawa, K. Inoue and H. Inouye, 'Absolute configuration and structure of carminic acid existing as the potassium salt in *Dactylopius cacti* L.', *Acta Crystallographica*, section C, Vol. 43 (8), 1987, pp. 1541–4.
  - 12 N.M. Barcenas and G. Aquino, 'In Vitro Culture of *Dactylopius coccus* Costa (Homoptera: Dactylopiidae): Potential Production of the Natural Dye Carminic Acid', *In Vitro Cellular and Developmental Biology*, 33, 1997, p. 21A (abstract of Symposium paper).
  - 13 See, for example, Schützenberger 1867 (cited in note 3), Vol. 2, p. 356; J.C. Leuchs, *Traité complet des propriétés, de la préparation et de l'emploi des matières tinctoriales, et des couleurs, traduit de l'allemand*, 2 vols, Paris 1829 (German edn published 1825), Vol. 2, p. 137.
  - 14 Leuchs 1829 (cited in note 13), Vol. 2, p. 137. The 1656 publication is attributed to 'Homberg' by Leuchs and several others, but as Wilhelm Homberg (1652–1715) would have been four years old at the time either the attribution or the date must be incorrect.
  - 15 M.P. Merrifield, *Original Treatises dating from the XIIIth to XVIIIth Centuries on the Arts of Painting*, 2 vols, London 1849 (reprinted New York, Dover, 1967), Vol. II, *Ricette per far ogni sorte di colore* (Padua, Biblioteca Universitaria, MS 992), pp. 698–9, 702–3, 708–9.
  - 16 See, for example, N. Catherinot, *Traité de la peinture*, Bourges 1687 (rep. Minkoff, Geneva 1973), p. 10.
  - 17 W. Homberg, [on the method of making carmine], *Histoire de l'Académie Royale des Sciences, depuis 1686 jusqu'à son renouvellement en 1699*, II, 1733, pp. 237–8; *Encyclopédie ou Dictionnaire raisonné des sciences, des arts et des métiers ... mis en ordre et publié par M. [D.] Diderot ... et M. [J.] d'Alembert*, 17 vols, Paris 1751–65, Vol. II, part 2 (rep. Geneva 1772), pp. 688–9. See also, for example, [P.A.] le Pileur d'Apligny, *Traité des couleurs matérielles, et de la manière de colorer, relativement aux différens arts et métiers*, Paris 1779, pp. 38–40.
  - 18 J.H. Pflingsten, *Farbenmaterialen, Eine vollständige Sammlung brauchbarer Abhandlungen und Erfahrungen für Künstler und Fabrikanten die mit Farben zu thun haben*, Berlin 1789, pp. 30–1; C.F.A. Hochheimer, *Chemische Farben-Lehre, oder ausführlicher Unterricht von Bereitung der Farben in allen Arten der Malerey*, Leipzig 1792, pp. 76–84. Hochheimer gives the sources for his recipes; for the method with alum, followed by a second precipitation with tin salts, he cites the apothecary Jacob Reinbold Spielmann's *Institutiones chemiae*, Strasbourg 1763.
  - 19 Cardon 2003 (cited in note 4), pp. 51–2.
  - 20 *Sehr geheim gehaltene und nunmehr frey entdeckte experimentirte Kunst-Stuecke, Die schoensten und raresten Farben zu verfertigen ...*, Zittau and Leipzig 1756, pp. 1ff. The authors would like to thank Frauke Schott and Mark Richter, Lehrstuhl für Restaurierung, Kunsttechnologie und Konservierungswissenschaft, Technische Universität, Munich, for this reference. Later sources include L. Marcucci, *Saggio analitico-chimico sopra i colori minerali e mezzì di procurarsi gli artefatti gli smalti e le vernici*, 2nd edn, Rome 1816 (1st edn 1813), p. 177.
  - 21 R. Dossie, *The Handmaid to the Arts*, 2 vols, London 1758, Vol. I, pp. 54–5; Neri/Merret 1662 (cited in note 10), p. 348 (incomparable Bow-dyes); J.M. Cröker, *Der wohl anführende Mahler*, Jena 1736 (facsimile reprint Mäander, Mittlenwald 1982), p. 106.
  - 22 [P.A.] le Pileur d'Apligny, *L'Art de la teinture des fils et étoffes de coton ...*, Paris 1776, p. 54.
  - 23 See, for example, Leuchs 1829 (cited in note 13), Vol. 2, p. 145; J. Lefort, *Chimie des couleurs pour la peinture à l'eau et à l'huile*, Paris 1855, p. 185.
  - 24 Hochheimer 1792 (cited in note 18), pp. 82–4; Leuchs 1829 (cited in note 13), Vol. 2, pp. 141–3.
  - 25 P.J. Pelletier and J.B. Caventou, 'Examen chimique de la Cochenille et de sa matière colorante', *Annales de Chimie et de Physique*, 8, 1818, pp. 250–86.
  - 26 J.F.L. Mérimée, *De la peinture à l'huile*, Paris 1830, pp. 124–5. See also, for example, J.F.D. Riffault Deshêtres, A.D. Vergnaud and C.J. Toussaint, *Nouveau manuel complet de fabricant de couleurs et de vernis*, new edn, ed. F. Malepeyre and E. Winckler, 2 vols, Paris 1884, pp. 159–60.
  - 27 J.H. Townsend, 'The materials of J.M.W. Turner: pigments', *Studies in Conservation*, 38, 1993, pp. 231–54, esp. pp. 240–1. The IR spectrum of the carmine suggests that it is a lake on a light alumina hydrate-type substrate.
  - 28 Dossie 1758 (cited in note 21), Vol. I, pp. 54–5.
  - 29 P. de La Hire, 'Traité de la pratique de la peinture', *Mémoires de l'Académie Royale des Sciences depuis 1666 jusqu'à 1699*, IX, Paris 1730, pp. 637–730, esp. p. 671. The text was given as a lecture to the Académie in 1709.
  - 30 S. Tschelnitz, *Farben-Chemie, insbesondere der Oel- und Wasserfarben nach ihren chemischen und physikalischen Verhalten, ihrer Darstellung und Verwendung*, Vienna 1857, pp. 103–4.
  - 31 It was also, like other carmines he tested, a 'Fine Carmine of W. Mortimer, prep<sup>d</sup> by him, very rich in the powder, works finely' and a 'Carmine of W. Ackerman (by Kerr)' extremely fugitive: G. Field, *Examples and Anecdotes of Pigments. Practical Journal 1809*, ff. 330, 355, 372. Papers of George Field (1804–1825), Field/6, photographic copy, Courtauld Institute of Art Library, London.
  - 32 The archives of Lewis Berger and Co. Ltd, paint manufacturers, Hackney, Middlesex, are held at the London Borough of Hackney Archives Department; see, for example, D/B/BER/1/2/3 Lake and Carmine Book, 1787–c.1830; D/B/BER/1/3/3, c.1829–1846; D/B/BER/1/3/5, c.1842–1907; see also S. Carew Reid, 'Lewis Berger & Sons (1766–1960): An English colour manufactory', 2 vols, 3rd Year Project carried out towards the Postgraduate Diploma in Conservation of Easel Paintings, Department of Conservation and Technology, Courtauld Institute of Art, London, 1997. The authors would like to thank Winsor & Newton, the Rijksbureau voor Kunsthistorische Documentatie (RKD) and the De Mayerne Programme for access to their Nineteenth-Century Archive project database.
  - 33 WN 16P011, on Berger's use of milk; WN 3PP244–5, 'No. 2 Crimson Batch, 7 October 1838', a cochineal lake: 'The tint ... was a complete match to Berger's.' © Winsor & Newton Archive, 2007.
  - 34 D/B/BER/1/2/3 Lake and Carmine Book (recipes dating from 1787 to 1815); D/B/BER/1/3/3, ff. 1–7; D/B/BER/1/3/5, ff. 53–6.
  - 35 G. Field, *A Journal of Practical Essays, Experiments and Enquiries*, April 20th 1807, f. 182. Papers of George Field (1804–1825), Field/3, photographic copy, Courtauld Institute of Art Library, London; WN 4PP070A–B, W & N no. 2707 'French Carmine Exp<sup>ts</sup>. April 23, 1872' (protection against mould); WN P4P138–9, 1840 (on the additional weight of hydrated tin oxide). © Winsor & Newton Archive, 2007.
  - 36 For example WN A6P044B (23 April 1872). © Winsor & Newton Archive, 2007.
  - 37 Lefort 1855 (cited in note 23), p. 180; Lefranc et Cie, *Fabrique de couleurs et vernis, toiles à peindre... Prix courant* [catalogue], Paris 1858 (deleted), 1867 prices, p. 2.
  - 38 Leuchs 1829 (cited in note 13), Vol. 2, pp. 144–5.
  - 39 G. Favaro, C. Miliani, A. Romani and M. Vagnini, 'Role of photolytic interactions in photo-aging processes of carminic acid and carminic lake in solution and painted layers', *Journal of the Chemical Society, Perkin Transactions* 2, 2002, pp. 192–7.
  - 40 Pelletier and Caventou 1818 (cited in note 25), pp. 258, 261.
  - 41 N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Oxford 1984, p. 447.
  - 42 S.N. Meloan, L.S. Valentine and H. Puchtler, 'On the Structure of Carminic acid and Carmine', *Histochemie*, 27, 1971, pp. 87–95; H. Schweppe and H. Roosen-Runge, 'Carmine – Cochineal Carmine and Kermes Carmine', *Artists' Pigments: A Handbook of their History and Characteristics*, Vol. 1, ed. R.L. Feller, Washington and Cambridge 1986, pp. 255–83. Only one example of a carmine containing significant proportions of calcium and aluminium has been found so far: a watercolour cake made by the London colourman Rudolph Ackermann before 1825.
  - 43 When modern carmines and carmines produced in the laboratory following recipes such as those given in Table 2 are examined in pure form, it is possible to distinguish Al-, Al/Ca- and Sn-containing carmines, but when these are combined with binding media and extenders the distinction is more problematic.
  - 44 Hochheimer 1792 (cited in note 18), pp. 84–97; Leuchs 1829 (cited in note 13), Vol. 2, pp. 147–51.
  - 45 See also J. Wouters, 'Notes on the Biology, History, Geography and Analysis of Insect Red Dyes and Pigments', in *Historical Polychromy: Polychrome Sculpture in Germany and Japan*, eds M. Kühnenthal and S. Miura, Munich 2004, pp. 380–92 (text in German and English) where only cochineal and

- traces of brazilwood are reported in eighteenth-century German polychromy.
- 46 Kirby, Spring and Higgitt 2005 (cited in note 6), pp. 72–5 and pp. 78–81.
  - 47 Kirby, Spring and Higgitt 2005 (cited in note 6), pp. 76–8.
  - 48 W.C. McCrone and J.G. Dely, *The Particle Atlas*, Vol. 2: *The Light Microscopy Atlas*, 2nd edn, Michigan 1973, pp. 457–62.
  - 49 A.S. Marggraf, [‘Verfertigung einer dauerhaften rothen Farbe für die Mahler, welche verlohren gegangen war und wieder entdeckt ist’], *Nouveaux mémoires – Académie royale des sciences et belles lettres, Berlin*, 1771 volume, 1773, p. 3 ff; see also Pflingsten 1789, pp. 267–9, Hochheimer 1792, pp. 104–5 (both cited in note 18).
  - 50 Neri 1612 (cited in note 10), p. 102.
  - 51 J. Kirby and R. White, ‘The Identification of Red Lake Pigment Dyestuffs and a Discussion of their Use’, *National Gallery Technical Bulletin*, 17, 1996, pp. 56–80; Kirby, Spring and Higgitt 2005 (cited in note 6); J. Kirby, D. Saunders and M. Spring, ‘Proscribed pigments in northern European Renaissance paintings and the case of Paris red’, *The Object in Context: Crossing Conservation Boundaries, Contributions to the IIC Munich Congress, 28 August – 1 September 2006*, eds D. Saunders, J.H. Townsend and S. Woodcock, London 2006, pp. 236–43.
  - 52 G. Field, ‘A Stove for heating Rooms or Drying different Articles’, *Transactions of the Society of Arts*, XXIV, 1806, pp. 129–33; G. Field, ‘Apparatus for Preparing Coloured Lakes’, *Transactions of the Society of Arts*, XXXIV, 1817, pp. 87–92; R. Bubb, ‘The life and work of George Field, colourmaker (1777–1854)’, in H. Althöfer (ed.), *Das 19. Jahrhundert und die Restaurierung. Beiträge zur Malerei, Maltechnik und Konservierung*, Munich 1987, pp. 238–47.
  - 53 Leuchs 1829 (cited in note 13), Vol. 2, pp. 153–4; P.F. Tingry, *The Painter’s and Colourman’s Complete Guide ...*, 3rd edn, London 1830, pp. 120–1.
  - 54 G. Field, *Rubia. Experiments on madder 1804*, ff. 184–6, 841–8. Papers of George Field (1804–1825), Field/1, photographic copy, Courtauld Institute of Art Library, London.
  - 55 L. Carlyle, *The Artist’s Assistant: Oil Painting Instruction Manuals and Handbooks in Britain 1800–1900 ...*, London 2001, pp. 157–60, 489–90, 501–2, 508–10.
  - 56 Travis 1994 (cited in note 1); Cardon 2003 (cited in note 4), pp. 101–8.
  - 57 Lefort 1855 (cited in note 23), p. 167; Schützenberger 1867 (cited in note 3), Vol. 2, p. 82.
  - 58 J.J. Colin and P.J. Robiquet, ‘Nouvelles recherches sur la matière colorante de la garance’, *Annales de chimie et de physique*, 2e série, 34, 1827, pp. 225–53; G. Ramunni, ‘Les Annales de chimie et de physique et les colorants: recherches et discussions’, in *Natural Dyestuffs and Industrial Culture in Europe 1999* (cited in note 1), pp. 25–42; Travis 1994 (cited in note 1), pp. 7–8; Schützenberger 1867 (cited in note 3), Vol. 2, pp. 107–13.
  - 59 Schützenberger 1867 (cited in note 3), Vol. 2, p. 121.
  - 60 Carlyle 2001 (cited in note 55), p. 508.
  - 61 On garancine see ‘Mémoire de MM. Robiquet et Colin sur la question, “Séparer la matière colorante de garance, et déterminer la quantité qu’un poids donné de garance peut en contenir”’, *Bulletin de la Société industrielle de Mulhouse*, 1828, pp. 126–45; Schützenberger 1867 (cited in note 3), Vol. 2, pp. 146–50.
  - 62 Lefort 1855 (cited in note 23), pp. 172–3.
  - 63 Schützenberger 1867 (cited in note 3), Vol. 2, pp. 158, 170.
  - 64 E. Kopp, ‘Recherches sur la garance d’Alsace’, *Répertoire de chimie appliquée*, III, 1861, pp. 85–97; Travis 1994 (cited in note 1), pp. 14–16; Schützenberger 1867 (cited in note 3), Vol. 2, pp. 160–3, 171.
  - 65 Mérimée 1830 (cited in note 26), pp. 144–63.
  - 66 Leuchs 1829 (cited in note 13), Vol. 2, pp. 155–8.
  - 67 Lefort 1855 (cited in note 23), p. 173; see also Schwartz’s procedure, which gave a brick-red product, Schützenberger 1867 (cited in note 3), Vol. 2, p. 153.
  - 68 J. Kirby, K. Stonor, A. Roy, A. Burnstock, R. Grout and R. White, ‘Seurat’s Painting Practice: Theory, Development and Technology’, *National Gallery Technical Bulletin*, 24, 2003, pp. 4–37, esp. p. 26.
  - 69 Lefranc et Cie 1858, 1867 prices (cited in note 37), pp. 2, 4–5.
  - 70 Boron trifluoride/ methanol breaks up the polymerised paint film by demethylation, also dissolving out the dyestuff from the lake pigment. It has the disadvantage of methylating vulnerable groups, such as the carboxylic acid group of carminic acid, to some extent, giving a peak for the methylated derivative as well as one for the original constituent. Quantitative examination of the dyestuff components is therefore rendered more difficult. See Kirby and White 1996 (cited in note 51), p. 60. HPLC analysis was carried out using Hewlett-Packard (now Agilent) HP1100 series binary pumps, modified for use with a capillary microbore column by the insertion of an ASI binary fixed flow 9:1 stream splitter (supplied by Presearch) between the pumps and the injector. This reduces a flow rate of 100  $\mu\text{l min}^{-1}$  at the pump to 10  $\mu\text{l min}^{-1}$  at the injector. The eluents used were (A) 99.9% water/ 0.1% trifluoroacetic acid, (B) 94.9% acetonitrile/ 5% methanol/ 0.1% trifluoroacetic acid; solvents were degassed by an HP1100 series vacuum degasser. The elution gradient programme was as follows: initial concentration of B 5%, held for 5 minutes; 5–25% B in 80 minutes; 25–50% B in 75 minutes; 50–95% B in 30 minutes; held at 95%B for 30 minutes; 95–5% B in 5 minutes; total run time 225 minutes, 15 minutes post run equilibration time. A Targa 150×0.5 mm i.d. column, Silica type B bonded phase C18 packing, 5  $\mu\text{m}$  particle size, maintained at a temperature of 40 °C (HP1100 column oven) was used, injecting samples manually through a Cheminert™ Valco injector (model INJ-P6; LC Packings, supplied by Presearch), fitted with a 2  $\mu\text{l}$  sample loop. Detection was performed using an HP1100 Diode array detector, monitoring signals at 254, 275, 330, 491 and 540 nm, set to record in 2 nm steps, reference 700 nm; band width 8 nm; flow cell path length 10 mm, 0.5 l volume, 4 nm slit width. HP Chemstation software (revision A.10.02) was used to control the equipment and process the data.
  - 71 A. Burnstock, I. Lanfear, K.J. van den Berg, L. Carlyle, M. Clarke, E. Hendricks and J. Kirby, ‘Comparison of the fading and surface deterioration of red lake pigments in six paintings by Vincent van Gogh with artificially aged paint reconstructions’, *ICOM Committee for Conservation, 14th Triennial Meeting, The Hague, 12–16 September 2005: Preprints*, ed. I. Verger, 2 vols, London 2005, Vol. I, pp. 459–66.
  - 72 This discussion refers to nineteenth-century madder lakes. Analysis has shown that madder pigments of the fifteenth to seventeenth centuries frequently contain a very high proportion of pseudopurpurin/purpurin, but these lakes are made by different methods: Kirby, Spring and Higgitt 2005 (cited in note 6), pp. 77–8.
  - 73 For a discussion of the pigments used in late paintings by Monet see the article by Ashok Roy in this volume of the *Technical Bulletin*, pp. 58–68.
  - 74 M. van Bommel, M. Geldof and E. Hendriks, ‘An investigation of organic red pigments used in paintings by Vincent van Gogh (November 1885 to February 1888)’, *ArtMatters, Netherlands Technical Studies in Art*, 3, 2005, pp. 111–37; A. Burnstock, K.J. van den Berg and J. House, ‘Painting techniques of Pierre-Auguste Renoir: 1868–1919’, *ArtMatters, Netherlands Technical Studies in Art*, 3, 2005, pp. 47–65; R. Boitelle, K.J. van den Berg and E. Goetz, ‘A technical examination of Odilon Redon’s paintings from the Bongor Collection, Van Gogh Museum’, *ArtMatters, Netherlands Technical Studies in Art*, 3, 2005, pp. 66–81. These authors have also identified starch in the pigments.
  - 75 Schützenberger 1867 (cited in note 3), Vol. 2, pp. 170–1.
  - 76 Typically the bands are seen at c.1590–80 with a shoulder around 1610, and at 1465 with a shoulder at 1410  $\text{cm}^{-1}$ .
  - 77 Samples of hydrated alumina and light alumina hydrate prepared in the laboratory and a commercial sample of extra bulky alumina hydrate (Lanabarc Ltd) all showed signs of reaction; aluminium sulphate and potassium aluminium sulphate did not, under the same conditions.
  - 78 A sample of aluminium stearate of unknown date and origin in the National Gallery laboratory collection shows bands at 1589, 1470 and 986  $\text{cm}^{-1}$ . The presence of an AlO–H vibration at 3692  $\text{cm}^{-1}$  suggests that this may be a basic aluminium stearate.
  - 79 Thanks are due to Katrien Keune for useful discussions about metal soap formation. See Kirby et al. 2003 (cited in note 68), p. 27.
  - 80 Kirby, Spring and Higgitt 2005 (cited in note 6), pp. 73–4.
  - 81 Pflingsten 1789 (cited in note 18), p. 38; Hochheimer 1792 (cited in note 18), pp. 97–100; Leuchs 1829 (cited in note 13), Vol. 2, pp. 151–3; Schützenberger 1867 (cited in note 3), Vol. 2, pp. 297–307.
  - 82 Riffault Deshêtres, Vergnaud and Toussaint 1884 (cited in note 26), pp. 137–8.
  - 83 Van Bommel, Geldof and Hendriks 2005 (cited in note 74), pp. 128–9.
  - 84 R.D. Harley, *Artists’ Pigments c. 1600–1835: A Study in English Documentary Sources*, 2nd edn, London 1982, pp. 133–4; E. Bancroft, *Experimental Researches concerning the Philosophy of Permanent Colours*, 2 vols, London 1813, Vol. II, pp. 1–59; Kirby and White 1996 (cited in note 51), pp. 70–3.
  - 85 A.G. Perkin and A. E. Everest, *The Natural Organic Colouring Matters*, London 1918, pp. 90–4; Cardon 2003 (cited in note 4), pp. 511–13.
  - 86 J. Hellot, *L’Art de la teinture des laines et des étoffes de laine en grand et petit teint*, Paris 1750, pp. 354–64; Schützenberger 1867 (cited in note 3), Vol. 2, pp. 343–8; A. Quye, H. Cheape, J. Burnett, E.S.B. Ferreira, A.N. Hulme and H. McNab, ‘An Historical and Analytical Study of Red, Pink, Green and Yellow Colours in Quality 18th- and Early 19th-Century Scottish Tartans’, *Dyes in History and Archaeology*, 19, 2003, pp. 1–12.
  - 87 Field/6 1809 (cited in note 31), ff. 331–2; Winsor & Newton Ltd Wholesale catalogue, n.d. [1870 or 1881], p. 65; 1886 Trade catalogue, p. 30; 1896 Trade catalogue, p. 77. © Winsor & Newton Archive, 2007.
  - 88 Unless it is a variety of *laque anglaise*: Lefranc et Cie 1858, 1867 prices (cited in note 37), p. 3 (four types). Only one variety appears in later catalogues

- (often only in powder form, not as tube colour) up to Lefranc et Cie, *Fabrique de couleurs et vernis, toiles à peindre* [catalogue], Paris 1890, p. 6 (tube colour).
- 89 Cardon 2003 (cited in note 4), p. 483.
- 90 Kirby and White 1996 (cited in note 51), p. 69; L. Keith and A. Roy, 'Giampietrino, Boltraffio and the Influence of Leonardo', *National Gallery Technical Bulletin*, 17, 1996, pp. 4–19, esp. p. 15 and note 39, p. 19.
- 91 Field/6 1809 (cited in note 31), f. 332.
- 92 S. Garfield, *Mauve: How One Man invented a Colour that Changed the World*, London 2000; M. de Keijzer and M.R. van Bommel, 'Bright new colours: the history and analysis of fluorescein, eosin, erythrosine, rhodamine B and some of their derivatives', paper presented at the 23rd Meeting of Dyes in History and Archaeology held at Agropolis International, Montpellier, 4–5 November 2004, in course of publication; see also Homburg 1983 (cited in note 1).
- 93 A.S. Travis, 'Heinrich Caro, chemist and calico printer, and the changeover from natural to artificial dyes', in *Natural Dyestuffs and Industrial Culture in Europe 1999* (cited in note 1), pp. 285–312; Nieto-Galan 2001 (cited in note 3), pp. 190–8.
- 94 G.H. Hurst, *Painters' Colours, Oils, and Varnishes: A Practical Manual*, 2nd edn, London 1896, pp. 288–91; F.H. Jennison, *The Manufacture of Lake Pigments from Artificial Colours*, London 1900, pp. 92–5.
- 95 Winsor & Newton Trade catalogue 1896, p. 77. © Winsor & Newton Archive, 2007.
- 96 Hurst 1896, pp. 272–90; Jennison 1900 (both cited in note 94). We are grateful to Maarten van Bommel, ICN, Amsterdam, for clarification of the composition of methyl violet.
- 97 Lefranc et Cie 1890 (cited in note 88), p. 5.
- 98 J.P. Rioux, 'Caractérisation de pigments décolorés dans les tableaux de Van Gogh peints à Auvers-sur-Oise', in *ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, 29 August–3 September 1999: Preprints*, ed. J. Bridgland, London 1999, pp. 402–8; J.P. Rioux, 'La décoloration de couleurs roses et pourpres dans les tableaux de Van Gogh peints à Auvers-sur-Oise', in *Un ami de Cézanne et Van Gogh, le docteur Gachet*, exh. cat. Paris: Galeries nationales du Grand Palais; New York: Metropolitan Museum of Art; Amsterdam: Van Gogh Museum, Paris 1999, pp. 70–82. Methyl violet has also been identified as a constituent of one of his paints: Van Bommel, Geldof and Hendriks 2005 (cited in note 74), p. 129.
- 99 F. Schott, 'Ein Reliquienschein des 18. Jahrhunderts: Studien zur Gestaltung und Technik', Diplomarbeit 2006, Lehrstuhl für Restaurierung, Kunsttechnologie und Konservierungswissenschaft, Technische Universität, Munich, 2006. We are very grateful to Mark Richter and Frauke Schott for providing us with this information.

**Table 1a. Results of analyses of red lake pigments in eighteenth-century paintings by optical microscopy, SEM-EDX, FTIR and HPLC**

Painting, title and date	Description of sample	Analysis of red lake pigment
Pompeo Girolamo Batoni, <i>Portrait of Richard Milles</i> (NG 6459), probably 1760s	Red of sitter's breeches. Red lake, bone black, vermilion.	HPLC: cochineal (New World: dcII). EDX: large Al, medium S (1/2 peak height of Al), small K. Pb soaps throughout. FTIR: sulphate present.*.**
Canaletto, <i>Venice: The Feast Day of Saint Roch</i> (NG 937), c.1735 <sup>1</sup>	Pale mauve-pink of drape by the window nearest the left edge. Red lake and round, colourless grains visible under the microscope.	HPLC: cochineal. EDX: large Al, small S, P, Si, K, Ca, Cl. FTIR: starch and other oval grains containing protein.
Canaletto, <i>A Regatta on the Grand Canal</i> (NG 4454), c.1740	Deep purple-mauve velvet on a gondola on the right of the painting. Red lake and a little lead white; round, colourless grains of starch visible under the microscope.	HPLC: cochineal. EDX: large Al, small S, P, Si, Ca, Cl. FTIR: starch (also polarised light microscopy).**
François-Hubert Drouais, <i>Le Comte de Vaudreuil</i> (NG 4253), 1758	Deep red area of chair back. Red lake, vermilion and black.	HPLC: cochineal. EDX: large Al, small Si, P, S, Cl, Ca. FTIR: very little sulphate, small amount of chalk, bands indicating hydrated alumina.
Thomas Gainsborough, <i>Dr Ralph Schomberg</i> (NG 684), c.1770 <sup>2</sup>	Pink area of coat. Red lake and a little lead white.	HPLC: cochineal (identified by microspectrophotometry). EDX: large Al, small S. FTIR: very little sulphate,* carmine bands with protein in a few deep pink particles.
Thomas Gainsborough, <i>Mrs Siddons</i> (NG 683), 1785 <sup>3</sup>	Mid-brownish red of curtain. Red lake, lead white, vermilion.	HPLC: cochineal. EDX: large Al, medium S (1/2 peak height of Al), small P, K, Ca. FTIR: sulphate present.*.**
Sir Thomas Lawrence, <i>Queen Charlotte</i> (NG 4257), 1789 <sup>4</sup>	Brownish-red foliage at the left of the painting.	HPLC: cochineal. FTIR: very little sulphate, carmine bands with protein in a few deep pink particles.**
Giovanni Antonio Pellegrini, <i>Rebecca at the Well</i> (NG 6332), 1708–13	Red cloak of the servant. Red lake.	HPLC: cochineal. EDX: large Al, small S, P, Si, Ca, K, Cl. FTIR: starch (also polarised light microscopy).*
Sir Joshua Reynolds, <i>Captain Robert Orme</i> (NG 681), 1756 <sup>5</sup>	Brightest red of coat. Vermilion, red lake and a little red earth.	EDX: Al, small S, Ca, K. FTIR: hydrated alumina, very little sulphate.*

Painting, title and date	Description of sample	Analysis of red lake pigment
Sir Joshua Reynolds, <i>Anne, 2nd Countess of Albemarle</i> (NG 1259), c.1760 <sup>6</sup>	Deep red of curtain. Red lake.	HPLC: cochineal. EDX: Al, medium S (1/2 peak height of Al). FTIR: carmine bands with protein in deeper pink areas of the sample, paler pink areas show more hydrated alumina substrate with sulphate.**
Sir Joshua Reynolds, <i>Lord Heathfield of Gibraltar</i> (NG 111), 1787 <sup>7</sup>	Red of coat. Large intense red lake particles, vermilion, red lead?	HPLC: – (colour suggests cochineal). EDX: rather low amount of Al. FTIR: carmine with protein. Protein content may account for large red lake particle size, unexpected for carmine.
Giovanni Battista Tiepolo, <i>An Allegory with Venus and Time</i> (NG 6387), c. 1754–8	Pink of the drapery of Venus. Lead white and red lake of large particle size.	HPLC: cochineal (New World: dcII). EDX: Al, large S (2/3 peak height of Al). FTIR: sulphate present.**
Claude-Joseph Vernet, <i>A Sporting Contest on the Tiber at Rome</i> (NG 236), 1750	Red of figure's jacket. Red lake and vermilion.	EDX: Al, large S (similar peak height to Al), significant amount of Ca. FTIR: sulphate present, as well as chalk.*
Attributed to Claude-Joseph Vernet, <i>A Seaport</i> (NG 1393), later 18th century	Deep mauve of drapery, lower left corner. Red lake and black.	EDX: Al, medium S (1/2 peak height of Al), significant amount of K. FTIR: sulphate present.*

\*: evidence of reaction between the binding medium and the substrate detected by FTIR

\*\* : lead soaps detected by FTIR

- 1 D. Bomford and A. Roy, 'Canaletto's "Venice: The Feastday of S. Roch"', *National Gallery Technical Bulletin*, 6, 1982, pp. 40–3.
- 2 D. Bomford, A. Roy and D. Saunders, 'Gainsborough's "Dr Ralph Schomberg"', *National Gallery Technical Bulletin*, 12, 1988, pp. 44–57, esp. pp. 51–4; J. Egerton, *National Gallery Catalogues: The British School*, London 1998, pp. 102–7.
- 3 Egerton 1998 (cited in note 2), pp. 114–19.
- 4 Egerton 1998 (cited in note 2), pp. 194–9.
- 5 Egerton 1998 (cited in note 2), pp. 206–9.
- 6 Egerton 1998 (cited in note 2), pp. 200–5; D. Saunders and J. Kirby, 'Light-induced colour changes in red and yellow lake pigments', *National Gallery Technical Bulletin*, 15, 1994, pp. 79–97, esp. pp. 79–80.
- 7 Egerton 1998 (cited in note 2), pp. 228–33.

**Table 1b. Results of analyses of red lake pigments in nineteenth-century paintings by optical microscopy, SEM-EDX, FTIR and HPLC**

Painting, title and date	Description of sample	Analysis of red lake pigment
Attributed to Pierre Andrieu, <i>Still Life with Fruit and Flowers</i> (NG 6349), probably c.1850–64	Dark red glazy paint from middle of top edge. Red lake, a little bone black, vermilion and siliceous iron earth pigment.	HPLC: madder, trace of cochineal. EDX: large Al, large P and S, suggests the addition of phosphate during manufacture. FTIR: sulphate and phosphate present.
Paul Cézanne, <i>An Old Woman with a Rosary</i> (NG 6195), c.1895–6	Lilac-grey in top left corner of the background. Lead white, red lake associated with translucent, colourless, round starch particles, cobalt blue.	HPLC: – (colour suggests cochineal). EDX: Sn substrate. FTIR: starch (also polarised light microscopy).*
Paul Cézanne, <i>Bathers (Les Grandes Baigneuses)</i> (NG 6359), c.1894–1905	Deep bluish-purple outline around the bather at the right-hand side. Red lake, cobalt blue, lead white. Round, colourless grains of starch.	HPLC: – (colour suggests cochineal). EDX: Sn substrate. Starch (polarised light microscopy).
Imitator of Thomas Couture, <i>Caught by the Tide</i> (NG 4613), 1860–90	Greyish-blue paint of sky from left edge. Cherry-coloured red lake pigment associated with translucent, colourless, round starch particles, lead white, vermilion, French ultramarine, bone black and a brown organic pigment.	HPLC: – (colour suggests cochineal). EDX: Sn substrate, small amount of Ca. FTIR: starch (also polarised light microscopy).
Hilaire-Germain-Edgar Degas, <i>Princess Pauline de Metternich</i> (NG 3337), c.1865 <sup>8</sup>	Pink paint beneath green near the top edge. Cherry-coloured red lake associated with translucent, colourless, round starch particles, lead white.	HPLC: – (colour suggests cochineal). EDX: Sn substrate, small Al, P (at a level expected from dyestuff), S. FTIR: starch (also polarised light microscopy).
Hilaire-Germain-Edgar Degas, <i>Portrait of Elena Carafa</i> (NG 4167), c.1875 <sup>9</sup>	Dark red-brown paint of wall hanging, top edge. Red lake (orange fluorescence under UV light) vermilion, lead pigment and iron earth pigment.	HPLC; madder. EDX: large Al peak, medium S ( $1/2$ Al peak height), small P. FTIR: sulphate and a little phosphate present.*
Ferdinand-Victor-Eugène Delacroix, <i>Louis-Auguste Schwiter</i> (NG 3286), 1826–30	Dark red glaze from lining of the hat. Two red lake pigments, madder lake (pinkish-orange fluorescence under UV light), and a more crimson lake (probably cochineal) associated with translucent, colourless, round starch particles.	HPLC: cochineal, madder. EDX: madder particles show large Al, some S, small Si, P, Ca. Darker red cochineal particles, Sn substrate. FTIR: starch (also polarised light microscopy). Smaller, darker red particles show carmine bands, with protein. Paler pink madder lake, sulphate present.*
Ferdinand-Victor-Eugène Delacroix, <i>Ovid among the Scythians</i> (NG 6262), 1859	Green paint from just below the basket at the lower edge over orange-brown paint containing French ultramarine, red lake (associated with translucent, colourless, round starch particles), orange earth and small amounts of other pigments.	HPLC: – (colour suggests cochineal). EDX: Sn substrate, small Al, P. FTIR: starch.
Paul Delaroche, <i>The Execution of Lady Jane Grey</i> (NG 1909), 1833 <sup>10</sup>	Red of executioner's calf. Red lake.	HPLC: cochineal. EDX: large Al, small Ca, K, Si, P.

Painting, title and date	Description of sample	Analysis of red lake pigment
Henri-Joseph Harpignies, <i>The Painter's Garden at Saint-Privé</i> (NG 1358), 1886	Deep red flower from above wall on the left side of the painting. Bright crimson red lake.	HPLC: – (colour suggests cochineal). EDX: colourless particles of chalk as extender not substrate. FTIR: carmine bands and chalk.
Ignace-Henri-Théodore Fantin-Latour, <i>The Rosy Wealth of June</i> (NG 1686), 1886	Red paint of the large red rose.	HPLC: – (orange fluorescence under UV light suggests madder). EDX: large Al, large S, small P. FTIR: sulphate present.*
Ignace-Henri-Théodore Fantin-Latour, <i>A Basket of Roses</i> (NG 3726), 1890	Red rose on table. Red lake with strong orange-pink fluorescence under UV light, cobalt violet, vermilion, iron oxide, lead white.	HPLC: – (orange fluorescence under UV light suggests madder). EDX: large Al, medium S, some P (from dyestuff), trace amount of K. FTIR: sulphate present.***
Follower of Jean-François Millet, <i>Landscape with Buildings</i> (NG 6253), after 1860	Grey-blue sky from right-hand edge. Lead white, red lake associated with translucent, colourless, round starch particles, cobalt blue, black, vermilion, siliceous iron oxide.	HPLC: – (colour suggests cochineal). EDX: Sn substrate, small Al, P, Ca. FTIR: starch.
Claude-Oscar Monet, <i>The Gare St-Lazare</i> (NG 6479), 1877 <sup>11</sup>	Deep purple paint in the shadow of the roof. Two red lakes: one, crimson, associated with translucent, colourless, round starch particles and one with an orange fluorescence under UV light; lead white.	HPLC: – (colour of crimson particles associated with starch suggests cochineal; orange fluorescence of second red lake pigment under UV light suggests madder). EDX: crimson particles, Sn substrate; particles with orange fluorescence, large Al, medium S. FTIR: starch associated with crimson particles. Larger pale pink particles with orange fluorescence contain sulphate.*
Claude-Oscar Monet, <i>Lavacourt under Snow</i> (NG 3262), c.1878–81 <sup>12</sup>	Dark purplish paint, base of tall tree, right. Red lake with a little cobalt blue, viridian and lead white.	HPLC: cochineal. EDX: Ca in rounded particles around 20 µm in size, some Al in matrix between Ca particles. FTIR: chalk.
Claude-Oscar Monet, <i>Flood Waters</i> (NG 6278), c.1896	Purplish paint near right edge. Red lake (pinkish-orange fluorescence under UV light), a little vermilion, white and viridian.	HPLC: madder. EDX: large Al and S. FTIR: sulphate present.
Claude-Oscar Monet, <i>The Water-Lily Pond</i> (NG 4240), 1899	Red paint of signature.	HPLC: madder. EDX: large Al and S. FTIR: sulphate present.
Claude-Oscar Monet, <i>Irises</i> (NG 6383), c.1914–17 <sup>13</sup>	Deep purplish stroke of paint near bottom edge. Red lake (strong pinkish-orange fluorescence under UV light).	HPLC: madder. EDX: large Al, large S (same peak height as Al), small P, K, Ca. FTIR: sulphate present.**

**Table 1b continued. Results of analyses of red lake pigments in nineteenth-century paintings by optical microscopy, SEM-EDX, FTIR and HPLC**

Painting, title and date	Description of sample	Analysis of red lake pigment
Adolphe Monticelli, <i>Torchlight Procession</i> (NG 5009), probably 1870–86	Bright red from woman's dress. Red lake.	HPLC: alizarin. EDX: Mainly Ca, small Al, P, S, Si, Cu, Zn. FTIR: alizarin crimson with chalk extender.
Adolphe Monticelli, <i>Subject Composition</i> (NG 5010), probably 1870–90	Red paint from woman's dress. Red lake associated with translucent, colourless, round starch particles.	HPLC: cochineal. EDX: Sn substrate. FTIR: carmine bands, starch (also polarised light microscopy).
Adolphe Monticelli, <i>Still Life: Oysters, Fish</i> (NG 5013), c.1878–82	Dark cherry-red paint near right edge. Red lake associated with translucent, colourless, round starch particles.	HPLC: cochineal. EDX: Sn substrate. FTIR: starch (also polarised light microscopy).
Adolphe Monticelli, <i>Still Life: Fruit</i> (NG 5014), c.1878–82	Deep red paint from tablecloth. Red lake associated with translucent, colourless, round starch particles.	HPLC: cochineal. EDX: Sn substrate. FTIR: starch (also polarised light microscopy).
Adolphe Monticelli, <i>A Vase of Wild Flowers</i> (NG 5015), probably 1870–80	Deep red paint of one of the flowers. Red lake associated with translucent, colourless, round starch particles.	HPLC: cochineal. EDX: Sn substrate. FTIR: starch (also polarised light microscopy).
Gustave Moreau, <i>Saint George and the Dragon</i> (NG 6436), 1889–90	Red of drapery around Saint George. Red lake with a little siliceous iron oxide.	HPLC: cochineal. EDX: large Al, P, S. FTIR: sulphate and phosphate present.
Pierre-Auguste Renoir, <i>A Nymph by a Stream</i> (NG 5982), 1869–70	Brownish-red paint of background, right-hand side. Red lake associated with translucent, colourless, round starch particles, some lead white.	HPLC: – (colour suggests cochineal). EDX: Sn substrate, some Al, Ca, P and S. FTIR: carmine bands, starch (also polarised light microscopy).
Pierre-Auguste Renoir, <i>At the Theatre (La Première Sortie)</i> (NG 3859), 1876–7 <sup>14</sup>	Deep purplish-red paint from lower left edge. Red lake and a little cobalt blue.	HPLC: – (orange fluorescence under UV light suggests madder). EDX: large Al, S, very small K. FTIR: sulphate present.*
Pierre-Auguste Renoir, <i>The Umbrellas</i> (NG 3268), c.1881–6 <sup>15</sup>	Pinkish-brown coat of the figure in the background, right-hand side. Red lake associated with translucent, colourless, round starch particles.	HPLC: – (colour suggests cochineal). EDX: Sn substrate. FTIR: starch (also polarised light microscopy).

Painting, title and date	Description of sample	Analysis of red lake pigment
Pierre-Auguste Renoir, <i>Moulin Huet Bay, Guernsey</i> (NG 6204), c.1883	Translucent red from right-hand edge. Red lake associated with translucent, colourless, round starch particles, vermilion, emerald green, cobalt blue, and small amounts of other pigments.	HPLC: – (colour suggests cochineal). EDX: Sn substrate. FTIR: starch (also polarised light microscopy).
Georges Seurat, <i>Bathers at Asnières</i> (NG 3908), 1884 <sup>16</sup>	Deep purple-brown shadow of trousers. Madder (strong fluorescence under UV light) and cochineal, two separate lake pigments, with French ultramarine.	HPLC: cochineal and madder. EDX: large Al, S in the madder lake. FTIR: sulphate present in the madder lake.*
Georges Seurat, <i>The Channel of Gravelines, Grand Fort-Philippe</i> (NG 6554), 1890 <sup>17</sup>	Bright red paint from the centre of the left edge. Large particles of red lake (pinkish fluorescence in UV light), vermilion.	HPLC: madder. EDX: large Al and S. FTIR: sulphate present.*

\*: evidence of reaction between the binding medium and the substrate detected by FTIR

\*\*\*: lead soaps detected by FTIR

- 8 D. Bomford, S. Herring, J. Kirby, C. Riopelle and A. Roy, *Art in the Making: Degas*, exh. cat., The National Gallery, London 2004, pp. 62–7.
- 9 Bomford et al. 2004 (cited in note 8), pp. 116–19.
- 10 J. Kirby and A. Roy, 'Paul Delaroche: A Case Study of Academic Painting', *Historical Painting Techniques, Materials and Studio Practice: Preprints of a Symposium, University of Leiden, the Netherlands, 26–29 June 1995*, eds A. Wallert, E. Hermens and M. Peek, Los Angeles 1995, pp. 166–75, esp. p. 172.
- 11 D. Bomford, J. Kirby, J. Leighton and A. Roy, *Art in the Making: Impressionism*, London 1990, pp. 166–71, 201.
- 12 Bomford et al. 1990 (cited in note 11), pp. 182–7, 201.
- 13 See the article by Ashok Roy in this volume, pp. 58–68.
- 14 Bomford et al. 1990 (cited in note 11), pp. 152–7, 201.
- 15 Bomford et al. 1990 (cited in note 11), pp. 188–95, 201.
- 16 J. Kirby, K. Stonor, A. Roy, A. Burnstock, R. Grout and R. White, 'Seurat's Painting Practice: Theory, Development and Technology', *National Gallery Technical Bulletin* 24, 2003, pp. 4–37, esp. p. 26.
- 17 Kirby et al. 2003 (cited in note 16), p. 26.

Table 2. Examples of carmine recipes and approximate proportions of ingredients (based on conversion to metric equivalents)

Source, date	Recipe	Cochineal (ground)	Salt of organic acid	Alum	Tin salts	Alkali	Protein	Other	Notes
Leuchs 1829, Vol. 2, pp. 137–9	Carmine (1656)	5 drachms/ 5 lb water (16/ 2.5 l)	18 grains (1)					0.5 drachm kermes; 18 grains alder (bark?) (1.5; 1)	Earliest published recipe, according to Leuchs
<i>Histoire de l'Académie Royale des Sciences</i> ... II, 1733, pp. 237–8	Carmine (Homburg 1695)	5 gros/ 5 lb water (19/ 2.5 l)		18 grains (1)				0.5 gros <i>chouan</i> seed, 18 grains <i>autour</i> bark (2; 1)	
<i>Encyclopédie raisonnée</i> ... 1751–65, Vol. II, part 2, p. 688	Carmine	5 gros/ <i>chouan</i> water (19)		18 grains (1)				36 grains <i>chouan</i> seed; 18 grains <i>raucour</i> ( <i>roucou</i> ) bark (2; 1)	<i>Chouan</i> : <i>Anabasis tamariifolia</i> L.; <i>raucour</i> , <i>roucou</i> : <i>Bixa orellana</i> L., annatto
<i>Encyclopédie raisonnée</i> ... 1751–65, Vol. II, part 2, p. 688	Carmine	2 gros/ <i>chouan</i> water (15)	8 grains cream of tartar (1)	8 grains (1)				1 grain <i>chouan</i> seed/ 3 <i>chopines</i> water; 1 grain <i>autour</i> bark; 8 grains talc (0.1/ 3 l; 0.1; 1)	<i>Autour</i> unidentified; talc calcined and washed 3MgO.4SiO <sub>2</sub> . H <sub>2</sub> O
<i>Sehr geheim gehaltenene ... Kunst-Stucke</i> 1756, pp. iff.	Carmine	5 lb/ water (161)		1 Loth (1)	1 lb tin; 1 lb <i>aqua fortis</i> / 3 Loth salt (?)				Sn[IV] chloride formed 'tin solution'; proportion probably variable
Pfingsten 1789, pp. 30–1	Carmine	4 oz/ 8–12 lb water (16.5/ 0.5–1 l)	2 <i>Quentchen</i> cream of tartar (1)	8 scruples (1.5)					A second precipitate is obtained using tin solution
Hochheimer 1792, pp. 76–7	Carmine	1 oz/ water (11.5)		2 scruples (1)					A second precipitate is obtained using tin solution
Hochheimer 1792, pp. 82–4	Carmine (anon. French = Alyon)	1 lb/ 2.5 buckets water (26/ 1 l)		6 drachms (1)		5 drachms soda/ 1 <i>Nössel</i> water (1/ 0.05 l)	2 egg whites in 1 <i>Nössel</i> (0.5 l) water (0.01 l mixture)		A bucket is taken to be 9 litres, but this is arbitrary
Marcucci 1816, p. 177	Carmine by precipitation	2 oz/ 20 lb water (113/ 19 l)		10 grains Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> or K alum (1)	0.5 oz Malacca tin; 1.5 oz <i>aqua forte</i> / 2 <i>denari</i> sea salt (?)				Sn[IV] chloride formed 'tin solution'; proportion probably variable
Leuchs 1829, Vol. 2, pp. 141–2	Carmine (Alyon)	1 lb/ 2.5 buckets water (25.5/ 1 l)		6 drachms (1)		6 drachms soda/ 1 lb water (1/ 0.05)	2 egg whites/ 0.5 lb (0.25 l) water (0.01 l mixture)		

Leuchs 1829, Vol. 2, pp. 141–2	Carmine (Langlois)	1.5 lb/ 4 buckets water (23/ 1 l)		15 oz (14.5)		10 drachms soda (1)	5 whole eggs/ 2 lb (1 l) water (0.03 l mixture)		
Leuchs 1829, Vol. 2, pp. 142–3	Carmine + gelatin	36.5 parts/ water (36.5)		2.5 parts (2.5)		1 part KHCO <sub>3</sub> (1)	1 part fish glue/ water (1)	3 oz saltpetre (1)	1 lb (489.5 g) cochineal needs 5 buckets (45 l) water
Leuchs 1829, Vol. 2, pp. 144–5	Carmine (Mme Cenette, Amsterdam)	2 lb/ 6 buckets water (10.5/ 0.5 l)	4 oz <i>sel d'oseille</i> , oxalic acid (1.5)	60 grains (1)		tin; 1 lb <i>eau de part</i> / 1 oz sea salt (?)			
Leuchs 1829, Vol. 2, p. 145	Carmine (Chinese + tin salts)	20 oz/ 1 bucket water (204/ 3 l)		1 part (1)		soda or potash solution (1.5)			Alkali added to precipitate the carmine
Leuchs 1829, Vol. 2, pp. 145–6	Carmine	16 parts/ 255 parts water (16)		1 part (1)					
Leuchs 1829, Vol. 2, p. 146	Inferior carmine	1 part	4–6 parts tin solution; 6 parts water (4–6/ 6)	ammonia till deep red (2)					
Mérimée 1830, pp. 124–5	Carmine	1 lb/ water (c. 29)		8–10 gros (2)		4–5 gros NaHCO <sub>3</sub> or KHCO <sub>3</sub> (1)			Refers to Pelletier & Caventou 1818
Pelouze 1840, Vol. 1, pp. 240–1	Liquid carmine	Dissolve in ammonia till solution red	acetic acid			ammonia		alcohol to accelerate precipitation	Carmine precipitated from ammoniacal solution with acetic acid; very pure
Riffault Deshêtres 1884, Vol. 2, pp. 159–60	Carmine (Wood 1856)	680 g (3)	225 g citric acid (1)	260 g (1)		250 g Na <sub>2</sub> CO <sub>3</sub> (1)			Soda solution + citric acid, add cochineal; filter

Sources cited are referenced in the text. Proportions in parentheses are based on conversion of weights to grams, volumes of water to litres; those for the solutions of tin salts cannot be estimated; those for egg protein are estimated for the mixtures with water.

Potash alum, potassium aluminium sulphate, AlK(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O  
 Aluminium sulphate, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>  
 Cream of tartar, potassium hydrogen tartrate, KOOOC(CHOH)<sub>2</sub>COOH  
 Soda, sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>  
 Bicarbonate of soda or potash, sodium or potassium carbonate, NaHCO<sub>3</sub>, KHCO<sub>3</sub>  
 Saltpetre, potassium nitrate, KNO<sub>3</sub>  
 Acetic acid, CH<sub>3</sub>COOH  
 Oxalic acid, HOOC-COOH·2H<sub>2</sub>O  
 Citric acid, HOOCCH<sub>2</sub>C(OH)(COOH)CH<sub>2</sub>COOH  
*Aqua fortis* (etc): nitric acid, HNO<sub>3</sub>; a mixture of this with common salt, NaCl, was commonly used to produce aqua regia (modern proportions usually 1 part concentrated nitric acid to 3 parts concentrated hydrochloric acid)