ART MATTERS

# A travel experience:

# THE COROT PAINTING BOX

## MATTHIJS MARIS AND 19TH CENTURY TUBE PAINTS

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### Introduction

Many museum collections contain painter's studio equipment, often obtained as part of an artist's bequest. Most of these objects remain hidden in the obscurity of the museums' storerooms. Sometimes, however, they are discovered and prove to be curious but important documents that illustrate the working practice of those artists who used them. Such is the small painting box owned by the Gemeentemuseum, The Hague, and attributed to the French painter Jean-Baptiste Camille Corot (1796-1875). According to the museum's documentation, the painting box was purchased in 1875 by the Dutch painter Matthijs Maris (1839-1917) at the auction of Corot's estate in Paris (fig. 1).[1]

In Corot's painting box seven small oil sketches are painted directly on the wood of the lid itself, each scene representing a moment in the painter's travels. The acceptance of Corot as the original owner of the box is primarily based on the stylistic attribution of these small oil sketches to the French master. Furthermore we know that Matthijs Maris, who was a great admirer of Corot, was in Paris in 1875.[2] And indeed, it would not be exceptional for a young artist to obtain such a souvenir from a much-admired older colleague.

fig.1 Corot's painting box, Gemeentemuseum Den Haag, Inv.no. MH 11 z,j.mb

Corot's painting box tells its own story. The scenes depicted and the painting technique provide many clues which substantiate the attribution to Corot. As we will show, the sketches are painted in the 1820s and possibly early 1830s, which means that the paints used were from the 'pre-tube' era. Analyses will disclose the early use of new and relatively expensive pigments.
There is more though. The compartments hold brushes, paint tubes from at least five different manufacturers, most of them 19th century, a small clip-on medium container, and two pushpins. Were these Corot's too, or did Maris use the box himself after, as we assume, acquiring it at the auction? The information gathered from the labels of the tubes, their dating and paint analysis leads to plausible answers to these questions. In fact two of the French tubes may have belonged to the old master, as they can be dated before 1880. However, we feel that it is more likely that his young admirer Maris added all the tubes as well as the brushes. Regardless of whether these materials actually belonged to Corot or came from Maris's studio, they provide an excellent and rare opportunity to study the material composition of a variety of well-preserved 19th century tube paints.

## Matthijs Maris

Matthijs Maris (1839-1917) studied at the Academy in The Hague and Antwerp. He travelled to Germany, France and Switzerland and sojourned in Paris with his brother Jacob from 1869 until 1871. Jacob left Paris in 1871 but Matthijs remained until 1877 when he moved to London where he worked until his death in 1917.[3] Thus he could have visited the 'Vente Corot' in 1875 and buy the painting box. Maris regarded Corot highly, and especially admired his later work. In a letter to Philippe Zilcken in 1892, he depicts Corot as follows: 'He tried to get a song passed through his leaves and elegant stems rising in the air coming from nowhere than his own imagination. Nature was only medium to express his imagination.'[4] Ernest D. Fridlander, a friend of Maris, writes in his biography: 'The painters of the school of Barbizon made strong appeal on him, but of these it was Corot that he oftenest talked ... One day we were speaking of him, Matthew Maris made reference to his stiffness and tightness of his early work... He loved the poetry, the looseness, and the tender quality of his maturer painting, and possessed a print of his "Souvenir d'Italie" which, in the extreme careless ease of its execution greatly pleased him...'[5]
Fridlander also describes Maris's London studio in great detail: 'Within the space between the screen, the fireplace and the window, and at an angle to the latter, there stood the master's easel, always in the same position, an old oil colour box beneath it...'[6] After Matthijs's death the contents of the studio came into the possession of Mrs. Isabella van Wisselingh-Angus, widow of the art dealer Elbert Jan van Wisselingh.[7] She brought the objects to the Netherlands where they were exhibited for some time in the Rijksacademie in Amsterdam. On a photograph of this 'Thijs-Maris-Memorial-Room' a painting box is placed beneath the easel just as Fridlander described (fig. 2). The box is open; a palette and some brushes as well as the little oil sketches in the lid can be discerned. The unknown reporter who wrote the short accompanying text pays no attention to the sketches at all, and speaks about 'his [Maris] painting box.'[8] The article breathes the almost religious admiration given to Matthijs Maris at that time, which may have obstructed a clear view of certain details. It is not known how long this memorial room existed, but sometime in the early 1920s the objects arrived at the Gemeentemuseum.[9]
Given the history of the painting box and its position in Maris' studio, one wonders whether Maris used it himself. Unlike Corot, Matthijs Maris was not a real landscapist and only in his early career, up till the 1860s, did he occasionally paint outdoors. It is therefore unlikely that he actually used the box to paint *en plein air* in his London period. However, he may well have put it to use in his studio as storage for his paints and brushes.

## Jean-Baptiste Camille Corot and open-air painting

### · *Introduction*

Most of the small oil sketches in Corot's painting box are typical examples of open-air painting and may be ranked among the sketches made in Corot's early career, in the 1820s and early 1830s, as they correspond in style and subject matter with the studies made during his travels to Normandy and Italy in those years. Late 18th century and early 19th century academic practice did allow studies after nature, but these were kept private and could be used in the studio execution of imaginary, historical landscapes. It would take until the end of the 19th century for open-air painting to become an art form in its own right. The Academy's acceptance of the *esquisse en paysage* as part of the painter's education in the early 1820s, marks the beginning of this process and more specialist equipment was developed for the open-air painter, such as lightweight field easels, portable painting boxes and the indispensable umbrella. Indeed, open-air painting became so popular that it was ridiculed in cartoons as well as by artists themselves like the painter Jules Breton who, working at Fontainebleau, describes the many artists' umbrellas in the fields as 'the flourishing of giant mushrooms'.[10]



fig. 2 The Maris-Memorial-Room at the Rijksacademie in Amsterdam in 1923. The painting box is placed underneath the easel, as in Fridlander's description.

fig. 3 Corot's Studio. On the walls many small landscape sketches

### · *Jean-Baptiste Camille Corot*

Corot began his painting career when he was 26 years old. A late-developer whose art became well respected by his contemporaries and the rising generation, the Impressionists. During the early 1820s Corot studied drawing at the Académie Suisse, and from 1822 when he became financially independent thanks to his parents' yearly allowance of fifteen hundred francs, he concentrated on painting. Landscape painting was his particular preference, and in 1822 he started his apprenticeship at Achille-Etna Michallon's studio. Michallon (1796-1822) had already travelled to Italy, and although belonging to the neo-classical tradition, emphasised the importance of open-air painting to his students. Corot's stay with Michallon, though cut short by the latter's untimely death in 1822, was important for his appreciation of the open-air oil sketch. He and his fellow-students were set to copy examples of the many open-air studies Michallon had made in Italy, including boldly sketched landscape elements and scenes in different lighting conditions.[11] After Michallon's death Corot became an apprentice in the studio of Jean-Victor Bertin. Bertin had been Michallon's master, and was a renowned landscape painter and teacher in Paris at that time. During his three years with Bertin, Corot copied botanical studies, examined the works of northern landscape painters, and drew and painted outdoors. From 1822 until 1825 he worked in Ville-d'Avray, Normandy and Rouen, and the forest of Fontainebleau. In one of his notebooks from 1825 he writes: 'I have noticed that all the work done at the first attempt is more honest, more pleasing in form, and that it was obvious then how to take advantage of contingencies; whereas in going back to it, that harmonious original touch often gets lost...'[12]
In 1825, he travelled to Italy. Although overwhelmed by the Italian light: '...this sun radiates a light that is discouraging. I feel the complete powerlessness of my palette',[13] Corot soon developed a free style of sketching in oils. With Pierre-Henri de Valenciennes (1750-1819) in mind, who in his treatise on landscape painting (1800)[14] advises the artist to use his time in Rome well 'harvesting' as many sketches and drawings as possible, Corot did exactly this and many of his Italian oil sketches and drawings would later decorate his Parisian studio walls (fig. 3). These open-air sketches were not meant as final art works. He never exhibited them but, sometimes, used them as reference and generously lent them to students and colleagues.[15] In general the sketches were made on paper which was later mounted on canvas. Robaut, who catalogued Corot's works in 1905, describes Corot's method: starting outdoors with a pencil sketch or a sketch in oils; after returning to his studio he elaborated on the sketch from memory; then he returned to the site to evaluate it before completing the sketch in his studio.[16] This was in fact the usual practice at that time. We feel, however, with Corot's own comment in mind, that many of the Italian oil sketches on paper were made *in situ* and were not (or only marginally) reworked in the studio. They were done quickly – as Valenciennes put it: 'rapidly made sketches, to catch nature red-handed.'[17]
Many artists used paper for their outdoor sketching escapades. Bouvier remarks (1827): 'Cartons and papers are only used to economise on canvas, either when one is a beginner in oil painting, or when one wishes to run around the countryside making some studies in oil after nature, without being too loaded and encumbered by stretchers.'[18] The paper was usually sized and prepared with a ground layer to prevent absorbency of the oil medium.[19]
Robaut recorded circa forty oil sketches from the period 1822-25, most of them on paper, all of a small horizontal format, many of which would have fitted perfectly in our painting box.[20] And indeed, the painting box shows many signs of intensive use: abrasion on all four corners at the bottom, probably from the stool or other support the box

fig. 4
Corot's painting box, bottom side. Abrasion on all four corners, probably from the stool or other support the box was placed on during use

fig. 5 a,b
(a) Pushpin holes in upper right corner of lid, (b) Pushpin holes in bottom right corner through the dress of the young woman



fig. 6
Corot painting outdoors, with umbrella, easel and painting box

fig. 7
Drawing by Alfred Robaut, Corot and his fellow artist Dutilleux, both sketching and painting outdoors, 1852; Corot is using his painting box as a support for his paper or cardboard

was placed on during use (fig. 4); the original handle has been replaced by a piece of string. There are many pushpin holes in the corners of the lid, most of them through the paint of the sketches (fig. 5a,b). There are also many traces of paint on the sketches caused by paint spilling slightly over the edge of the paper attached in the lid, as well as smudges from wet paint on the palette stored in the box. In the edges of the lid, paint has accumulated from regular use, most colours -mainly greens in the lower and blues in the upper halve- corresponding with the typical landscapist's palette. The measurements of the inside of the lid are 34,7 x 25 cm. The pushpin holes in the corners range from 34 x 23 cm to 28 x 20 cm. Some holes in other places show that Corot also used various vertical and low horizontal formats. From the early 1830s, formats tend to be larger. There are many photographs of Corot later in his career, sitting outside at his easel, dressed in an artist's smock, sheltered from the sun by a giant umbrella and with a painting box at his side. Callen feels that these pictures are posed to emphasise Corot's practice of open-air painting (fig. 6).[21] However, there also exist various drawings made by fellow artists who are known to have accompanied him on his escapades to the countryside, where we see him sketching or painting outdoors. It seems unlikely that these were just posed too. In a drawing by Alfred Robaut from 1852 we see Corot and his fellow artist Constant Dutilleux (1807-1865), both working outdoors. Corot is using a painting box similar to the one discussed in this article (fig. 7).

- *The sketches: identification*

It is in the context of Corot's early painting practice *en plein air* that we should look at most of the small sketches in the lid. We feel that their style corresponds with that of works made during Corot's visits to Fontainebleau and to Normandy – in particular to Honfleur and Rouen – in the years between 1822 and 1825, and during his first trip to Italy (1825-1828).[22] The image of Vesuvius seems to derive from Corot's Neapolitan stay of February – March 1828 (fig. 8). Not much information exists about his seven-week stay, but the image sketched in the lid of his painting box follows a similar composition as his oil sketch of Vesuvius (Louvre)[23] – although it shows the volcano under different circumstances – and a drawing in one of his sketchbooks from that trip.[24] From 1750 until 1850 Vesuvius was a frequent subject for landscapists, depicted by Valenciennes, Vernet, Michallon and many others. After the discovery of Pompeii and Herculaneum, Naples became a must see in strong competition with Rome.[25] In 1776 Sir William Hamilton published *Camphi Phlegraei*, a compilation of 54 hand-coloured engravings of volcanoes. This became



important material for scientists and artists alike.[26]
Although the Vesuvius was not active at the time of Corot's visit, he painted a dark threatening volcano with bright red lava and reddish fumes, set against an intense dark blue sky. After an increased activity of Vesuvius in the 18th century, there was a major eruption in 1822, the next came in 1834. Therefore, the depiction in the lid seems to be imaginary and brings to mind Valenciennes, who was in Italy in the late 18th century and saw the Vesuvius in the state depicted by Corot. In his treatise Valenciennes devotes several pages to volcanoes, describing them as 'worthy to attract the attention of the artist and to put his brush to the test.'[27] He also says: 'The eruption of a volcano is the most terrible and magnificent spectacle that Nature can offer', and 'It is desirable that a painter can, once in his lifetime, witness the eruption of a volcano.'[28] The different paint handling of the volcano scene in comparison with the two small landscapes in the lid is partly due to the fact that (as we will see later) the scene covers another sketch. It may also be due to the subject itself as Valenciennes explains in his chapter on aerial perspective how '...the colour of the lava ..., offers saturated hues of red, yellow, brown or black; the volcanic mountains always seem to be closer than they actually are. This effect is very noticeable in Naples...'[29] It is likely that Corot saw sketches of Vesuvius by his first master Michallon and had the desire to depict an active volcano, hence this imaginary scene based on an outline of the real view.
The little seascape with an island in the distance could be Ischia, or possibly Capri (fig. 9).[30]
The two river views are more difficult to place. The larger sketch could have been made along the Seine near Rouen during one of Corot's visits to Normandy before or soon after his Italian trip (fig. 11). However, the fact that the paint of the Italian sketch of an island view partially overlaps the black border surrounding the central river scene, may indicate a date ante quem of 1828.[31] The same can be said about the small river scene (fig. 10), which in style and colour corresponds with for example *Little Chaville*, (c. 1825, 24 x 33 cm, Ashmolean Museum, Oxford) (fig. 12). The little fishermen's boat could also date from that time as Corot did visit Honfleur and its port many times in the early 1820s (fig. 13). Next to this another – unidentifiable – sketch can be discerned under the Vesuvius, with adjacent another sketch also partially covered by the Vesuvius, of what appears to be a sea view. It seems that there is also another sketch beneath the depiction of the young woman. These may also have been scenes from Normandy, depicted by Corot before his voyage to Italy.
That leaves the full-length female portrait of a young woman in a white dress carrying a bouquet of flowers

fig. 8
Vesuvius. In the centre of the volcano the vertical border of an underlying sketch can be discerned

fig. 9
Island view, Ischia or Capri?, centre left of the lid

fig. 10
Small river landscape in the left upper corner of the lid

fig. 13
Fishermen's boat, centre right of the lid

fig. 11
River Landscape in the centre of the lid

fig. 14
Female figure

fig. 12
J.B.C. Corot, Little Chaville, ca. 1825, oil on paper, 24 x 33 cm, Ashmolean, Oxford. One of Corot's early oil sketches that match the lid. Quite similar in style and use of colour as the small river landscape in the lid (see fig. 11)

-possibly a bride (fig. 14). Here we can only be speculative. Corot's first studies of figures seem to stem from his Italian sojourn, following the advice of Valenciennes and Michallon, who mention the need to record 'after nature' a variety of figures, costumes and poses, which could be used in landscapes.[32] The clumsiness of the figure suggests an early date. Many pushpin holes go through the paint layer and there are smudges of green paint on the surface, suggesting it was made at an early stage. Corot was never married, and in a letter to his friend Abel Osmond (Papigno, August 26, 1826) he writes: '...I have only one goal on life that I want to pursue with perseverance: to make landscapes. This firm resolution keeps me from a serious attachment...'33 However, in the same letter he speaks of Mademoiselle A., one of the milliners he met while working in his parents' business. Apparently she married someone else while Corot was away in Italy. In the same letter to his friend he says: 'I love this young person forever; but my independent character and the serious study, of which I need a great deal, make me take this situation lightly.'[34] Could this be a portrait of A. in her wedding dress? We can only guess.

## The Corot painting box: a technical examination

The arguments given above support our proposition that the sketches in the lid were made by Corot. We will now analyse the technique used in the sketches on the basis that they represent Corot's early oil sketching methods. The content of the box – which seems to be of a later date and were most likely Maris's – will be discussed in the paragraph on the technical examination of the tubes and brushes.

### *Corot's colourmen*

As we presume that Corot used the painting box in his early career, the box would then have contained paints in bladders, or dry pigments and containers with oils, this, as will be discussed further, does not contradict our findings. Corot bought materials from Colcomb-Bourgeois in Paris. During his first trip to Italy he asked his friend Abel Osmond to go to Colcomb-Bourgeois to see if they had good quality Antimony yellow: 'If it is good, take a pound (an ounce costs 2 francs), and also take three-quarter pounds of Mars yellow...'[35] This obviously concerns powder pigments. Colcomb-Bourgeois was renowned for its antimony yellow, Mars colours, cobalt blue and madder carmine.[36] It seems that Corot may have had a preference for some of their 'speciality' colours – we found ample use of cobalt blue in the sketches – but only if, as he insisted, the quality was good. However, on some of his later canvases stamps from Ottoz are present. Ange Ottoz opened his shop in 1827, the first in a long tradition of family businesses trading in artists' materials.[37] One would expect Corot to buy the materials most suited to his style of painting, and to buy from those colourmen who answered his needs.

### *The sketches: technique*

The technique of the sketches in the lid is in keeping with Corot's known sketches from those early years. They seem to be quick, wet-in-wet painted sketches, applied either directly on the wood of the lid, like the central river landscape, or on top of earlier sketches, like the Vesuvius. How do these compare with Corot's work at that time? Roy, in his article on the Barbizon painters, describes the myth around open-air painting and provides evidence of Corot's reworking in the studio of his open-air sketches. He explains how in Corot's small *études* on canvas, a more complex layer structure was found: not always wet-in-wet but with later revisions; sometimes even with a preliminary pencil sketch.[38] This corresponds with Robaut's description of Corot's working method, as mentioned above, and with documentation on the methods of other Barbizon painters at that time.[39] Corot himself described his method as follows: 'I have learned from experience that it is very useful to begin by drawing one's picture very purely on a blank canvas...next, to paint the picture part by part, each as finished as possible from the start, so as to have little left to do once the whole canvas is covered.'[40] These remarks, as well as Roy's results seem more applicable to his studio work. Nonetheless, a survey of his sketches on paper from the 1820s and 1830s shows some correspondence with the method described. It is easy to see how he painted each aspect, often in just one layer, creating a certain degree of finish but retaining a free manner. Corot was a pioneer as an artist who no longer worked with *clair-obscure* but focused on the light and its tonal values. He was, he said, 'looking for the form, the whole, the mass of tones', and his so-called *peinture blonde* contradicted the pictorial conventions that caused the unnatural appearance in studio landscapes. Corot is said to have added lead white to most of his paints to stabilise them and protect them from darkening.[41]

### *The sketches: painting materials*

If the sketches in the lid are dated correctly, the pre-tube paint Corot used could have been made either by the painter himself, from dry pigments, oil, and possible additives, perhaps even *in situ*, or have been bought in bladders ready-made from the colourman. The contents of the painting box could have looked much like, for example, Constable's paint box of 1837 (Manton Collection, New York), which



contains a phial of powdered smalt, a lump of gypsum, and eleven bladders with prepared oil paint.[42] Contemporary documents advise against keeping certain paints in bladders, like lake pigments, vermilion and more costly pigments like ultramarine, Indian yellow and 'others that one seldom uses.'[43] Bouvier states that these should preferably be kept as dry powders and mixed with oil only when a palette is being prepared and one is ready to start painting immediately.[44] He also proposes a portable grinding slab and a small muller to prepare paints for immediate use or when only small amounts are required. We can add to this the Dutch colourman Susse's description of a method of paint preparation 'while one is in the countryside or travelling', from powder pigments and a binding medium, using a palette and a glass muller.[45] Another source suggested that a palette could be prepared just before setting off to paint outdoors.[46]

In an attempt to identify the materials used by Corot, we took paint samples from seven areas in the sketches and one from the paint accumulated in the inner edge of the lid. The samples, numbered CL1-CL8, were partly made into cross-sections. These were analysed using light microscopy, and SEM-EDX. Additional analyses like Py-TMAH-GCMS, and FTIR were performed for identification of the binding media (see Table 3 Methods and techniques). The results are presented in Table 1 and in figs. 15-20.

The cross sections taken in the depiction of the young woman (fig. 15) and in the volcano (figs.19-20) confirm the presence of underlying sketches (CL1, 6, 5). The palette used in these (partially) hidden sketches hints at landscapes. Interestingly the double green layers in both hidden landscapes were applied wet-in wet, indicating a quick way of working by just adding an extra pigment to an existing mixture on the palette for a slightly different hue. It is unclear why Corot covered these little sketches: a particular motivation perhaps, such as we speculated on in the case of the young woman, or a whim to paint Vesuvius active. Two samples were taken in the greens of the central landscape – CL2 from the light green area on the hill in the centre (fig. 16) and CL3 from the dark green in the trees in the foreground (fig. 17). Here Corot painted directly on the wood of the lid, laying in single green layers, and using the warm brown colour of the wood as a dark tone. In the cross-section taken from the inner edge (top centre) of the painting box (CL4) at least seven paint layers are present showing a rather strange pattern which arises from the accumulation of paint applied beyond the borders of the sketches on paper and pushed into the inner edge of the lid (fig. 18). The lower whitish layers seem to have been applied while still malleable, the top blue layers were applied with some drying time in between. The layers show mainly blue hues, ranging from almost white to a darker blue, presumably corresponding with depictions of skies as can be expected in the top half of the box. The thin brownish layers in between may come from, for example, his small, Italian figure studies on paper.
In all, the paints studied show a complex use of pigments which underlines the reputation of Corot as an early tonal artist and seems to indicate a mixing of various prepared bladder paints, or powder pigments and oils, on the palette. It should also be remarked that many of the mixtures contain some addition of lead white, which would correspond with Corot's *peinture blonde* approach.

### *Some remarks*

A closer look at the pigments found in the cross-sections (Table 1) reveals a general use of relatively new and more expensive pigments like cobalt blue, Schweinfurt green, and possibly Florentine brown. Corot, thanks to his parents' generous allowance, was quite well off and could easily afford these more costly materials.
In the sketches Corot used some ultramarine, azurite and Prussian blue, but his main blue pigment is cobalt blue ($CoO.Al_2O_3$). Thénard discovered this bright blue colour in 1802. It was soon manufactured commercially and, though costly, used by many artists. Merimée mentioned it in 1830, and Winsor & Newton listed it from 1840, both as tube paint and as powder.[47]
Various copper-based greens were found in the sketches. The most remarkable is Schweinfurt green, a copper acetoarsenite ($_3Cu(AsO_2)_2.Cu(CH_3COO)_2$), which was confirmed by SEM-EDX, indicating both copper and arsenic (CL1, CL5). PLM showed the typical green spherulitic morphology of the pigment. XRD indicated brochantite, basic copper sulfate that was used in the preparation of Schweinfurt green using the sulfate method (CL5), first published by the French chemist Braconnot in 1822.[48] Schweinfurt green was invented by Sattler and Russ in Schweinfurt in 1814. Although the pigment was available, its composition and production method was a trade secret until 1822, when its methods of preparation were made public by Von Liebig and Braconnot.[49] It provided an intense green colour, also known as Vert Veronese, and Emerald green. After 1822 it was manufactured widely. Winsor & Newton list it as Emerald green in their 1832 catalogue.[50] Townsend (1993) identified it in two watercolours by Turner from 1832.[51] It is not clear when this pigment became available to artists in France. Merimée mentions it in 1830; an indication that it must have been obtainable in France at that early time.[52] Perhaps it was bought from its German manufacturer and given to Corot by one of his companions; many foreign artists traveled to Normandy and Fontainebleau.


**fig. 15**
Cross-section CL1 taken from the bright red area in the volcano scene.
1) c. 45 $\mu$m layer of lead white and two different green pigments: Schweinfurt or Scheele's green and a second, unidentified, copper containing green. Little fine red pigment and cobalt blue;
2) c. 55 $\mu$m. Similar to layer 1, but more green particles; 3) c. 65 $\mu$m layer of vermilion and bone black, a little red ochre, organic red pigment and barium sulphate. Microscope magnification 200x, bright field illumination

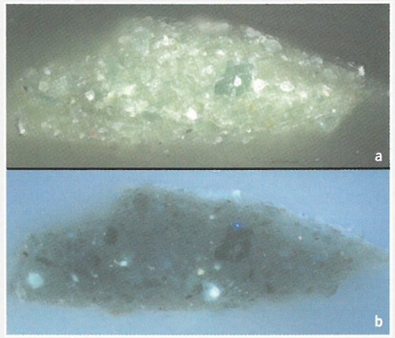


**fig. 16 a, b**
Cross-section CL2 taken from a bright green area on the hill in the central landscape.
1) c. 90 $\mu$m layer of green copper containing pigment, lead white, and little yellow ochre, barium sulphate, orange and brown-black particles. Presumably chalk is present as well. Some additional transparent particles show green fluorescence under UV. These particles contain aluminium. Microscope magnification 500x
a) bright field illumination
b) UV-fluorescence

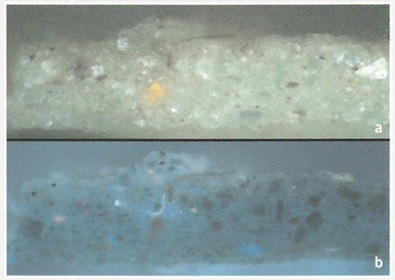


**fig. 17 a, b**
Cross-section CL3 taken from a dark green area in the trees in the central landscape.
1) c. 70 $\mu$m layer containing green copper containing pigment, quartz, chalk and little cobalt blue, pink fluorescing organic red (on an aluminium containing substrate) and minium. In addition, unidentified red, brown and white particles are present.
Microscope magnification 500x
a) bright field illumination
b) UV-fluorescence

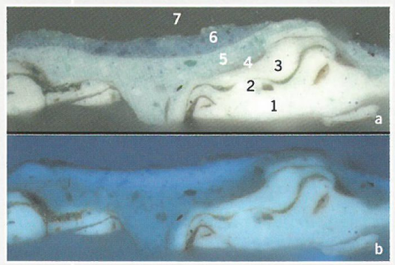


**fig. 18 a, b**
Cross-section CL4 taken from blue paint in the inside of the edge of the lid of the painting box.
1) c. 70 $\mu$m layer of lead white and little ultramarine;
2) c. 8 $\mu$m layer with yellow and orange fluorescencing, yellow particles in brown medium; 3) c. 30 $\mu$m. Similar to layer 1, but in addition little black and red pigment;
4) c. 6 $\mu$m layer of brown, red and white particles in brown medium;
5) c. 40 $\mu$m light blue layer of cobalt blue, lead white, copper containing green and a few transparent particles;
6) c. 30 $\mu$m dark blue layer containing cobalt blue, lead white and a few orange particles; 7) 8 $\mu$m greyish material on top.
Microscope magnification 200x
a) bright field illumination b) UV-fluorescence.

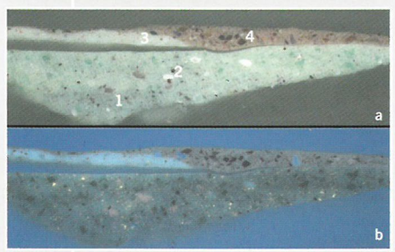


**fig. 19**
Cross-section CL5 taken from the reddish brown background in the woman scene.
1) c. 60 $\mu$m. Similar to layer 2, but in addition presumably Prussian blue is present;
2) c. 70 $\mu$m layer of lead white, a copper containing green and Schweinfurt green. In addition two kinds of organic red pigments: pale red, pink-fluorescing particles on a substrate containing aluminium and dark red, non-fluorescing particles on a substrate which seems to contain calcium. Three different yellow pigments are present: a non-fluorescing unidentified yellow pigment, an orange fluorescing yellow pigment and a yellow fluorescing, organic yellow pigment on a substrate which seems to contain calcium;
3) c. 20 $\mu$m layer of lead white and little vermilion, cobalt blue, yellow ochre, bone black and unidentified red particles;
4) c. 30 $\mu$m layer containing red (copperferrocyanide red, see text), cobalt blue and yellow.
Microscope magnification 200x
a) bright field illumination b) UV-fluorescence

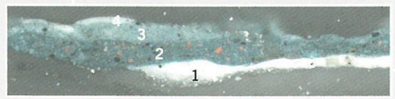


**fig. 20**
Cross-section CL6 taken from the blue sky in the volcano scene.
1) c. 20 $\mu$m layer of lead white and little bone black, orange fluorescing organic red pigment and cobalt blue;
2) c. 30 $\mu$m layer of fine dark blue pigment and coarser light blue particles, possibly Prussian blue and azurite respectively. In addition little bone black, lead white, barium s ulphate and vermilion;
3) c. 20 $\mu$m layer of copper containing blue, possibly azurite, and lead white;
4) c. 10 $\mu$m layer of lead white and little cobalt blue.
Microscope magnification 200x, bright field illumination



**Table 1.** Results of the analysis of paint samples taken from the sketches in the lid of Corot's painting box.

| Sample number, sample spot | SEM-EDX [1,2,3] | Other techniques [1,3,4] | Conclusions |
|---|---|---|---|
| CL1<br>Bright red area in the volcano scene. | *Layer 1:* Overall: Pb, Cu. Green particle: Cu, (P); Green particle: Cu, As; Blue particle: Al, Co<br>*Layer 2:* Overall: Pb, Cu, As. Green particles: Cu, As; Fine red particle: Pb, Sn, (Cu), (As), (Al), (P); Blue particle: Pb, Fe, (As), (K), (Cu)<br>*In between layer 2 and 3:* Black particles: Cu<br>*Layer 3:* Overall: Hg, S, (Ca). Black particle: Ca, P; Red particle: Fe, (Si); Particle: Ba, S | No analysis done. | *Layer 1:* Lead white, Schweinfurt/Scheele's green, copper green pigment and cobalt blue.<br>*Layer 2:* Lead white, Schweinfurt/Scheele's green, possibly organic red pigment and Prussian blue.<br>*In between layer 2 and 3:* Possibly copper oxide[5].<br>*Layer 3:* Vermilion, bone black, red ochre and barium sulphate. |
| CL2<br>Bright green from the central landscape. | *Layer 1:* Overall: Cu, Fe, (Al), (Si), (Pb), (Ca). Green particle: Cu; Yellow particle: Fe; White particle: Pb; Particle: Ba, S; Green fluorescing, transparent particle: Al, S, (Mg), (Cu) | No analysis done. | *Layer 1:* Copper green pigment, lead white, yellow ochre barium sulphate and presumably chalk. In addition a few particles that contain mainly aluminium. |
| CL3<br>Dark green from the central landscape. | *Layer 1:* Overall: Cu, (Pb), (Al) Green particles: Cu; Red particle: Al, Cu, (S), (Ca); Yellowish particle: Cu, P, Fe, (Si); Blue particle: Al, Co | **XRD:**<br>*Pseudo*-malachite (copper phosphate hydroxide), chalk and quartz. | *Layer 1:* Copper green pigment, *pseudo*-malachite, cobalt blue, organic red pigment (on an aluminium containing substrate), minium, chalk and quartz. |
| CL4<br>Blue from the inside of the edge of the lid, top centre. | *Layer 1:* Overall: Pb. Blue particle: Al, Si, S, Na, Pb, (K)<br>*Layer 2:* Overall: (low signal in general) Pb, Al, Ca, Cu, (As), (Si), (Co)<br>*Layer 5:* Overall: Pb, Cu, (Al), (Co)<br>*Layer 6:* Overall: Al, Pb, Co, (Cu), (As), (Ni) | **Py-TMAH-GCMS:**<br>*Mainly layer 5 and 6*<br>P/S =3.3 > nut oil or mixture of oils, slightly heat-bodied (diFA C9/C8=4.6). | *Layer 1:* Lead white and ultramarine.<br>*Layer 2:* Mainly organic material.<br>*Layer 5:* Lead white, copper green pigment and cobalt blue.<br>*Layer 5 and 6:* Nut oil or (more probably) a mixture of oils, slightly heat-bodied.<br>*Layer 6:* Lead white, cobalt blue, Schweinfurt or Scheele's green and possibly copper green pigment. |
| CL5<br>Reddish brown background in the woman scene. | *Layer 1:* Yellow particle, orange fluorescing: Pb, (Fe), (K)<br>*Layer 1 and 2:* Overall: Pb, (Cu)<br>*Layer 2:* Red particle, pink fluorescing: Al, Pb, S, (K); Dark red particle, non-fluorescing: (low signal in general) Pb, (Al), (K), (Ca); Green particle: Cu, As; Yellow particle, yellow fluorescence: Pb, Ca, (As), (Fe), (Cu); Blue dot: Pb, K, Fe, (Cu)<br>*Layer 3:* Red particle: Hg, S; Black particle: Ca, P; Blue particle: Al, Co; Yellow particle: Pb, Fe<br>*Layer 4:* Red particles: K, Fe, Cu, (Pb); Blue particle: Al, Co, (Ni); Brown-red particle: Si, K, Fe, (Al) | **XRD:**<br>Lead white, brochantite (basic copper sulfate)[6].<br>**PLM:**<br>Green particles: spherulites, doughnut shape, anisotropic, consistent with reference sample of Schweinfurt green > Schweinfurt green | *Layer 1 and 2:* Schweinfurt green, basic copper sulphate, lead white, organic red pigment on an aluminium containing substrate, organic red pigment on possibly a calcium containing substrate, organic yellow pigment, on a calcium based substrate and presumably Prussian blue.<br>*Layer 3:* Vermilion, cobalt blue, bone black and yellow iron oxide.<br>*Layer 4:* Cobalt blue and possibly copper ferrocyanide red (Florentine brown).[7] |
| CL6<br>Blue sky of the volcano scene. | *Layer 1:* Overall: Pb, (Al) Red particle: Al, Pb, (Cl),(K),(Na); Blue particle: Al, Pb, Co<br>*Layer 2* Matrix: Pb, (Cu), (Ca), (Fe) Particle: S, Ba; Black particle: P, Ca, (Pb); Blue particle: Cu, (Pb); Red particle: Hg, S<br>*Layer 3:* Blue particle: Cu, (Pb); Green particle: Cu, (Pb)<br>*Layer 4:* Blue particle: Al, Pb, Co | **XRD:**<br>Lead white and cobalt blue.<br>**PLM:**<br>Blue particles: very fine isotropic > organic blue pigment. Red particles (organic): isotropic > organic red on isotropic substrate.<br>**Microchemical analysis:**<br>Treatment with NaOH-solution: no change observed > no Prussian blue present[8].<br>**Py-TMAH-GCMS:**<br>P/S =7 > poppy oil, not heat-bodied (diFA C8/C9=6). | *Layer 1:* Lead white, cobalt blue and organic red pigment on an aluminium containing substrate.<br>*Layer 2:* Copper blue pigment[9], bone black, barium sulphate, lead white, vermilion and possibly Prussian blue.<br>*Layer 3:* Copper blue pigment[9], copper green pigment and lead white.<br>*Layer 4:* Lead white and cobalt blue Blue paint contains poppy oil, not heat-bodied. |
| CL7<br>White clouds on the central scene. | No analysis done. | **Py-TMAH-GCMS:**<br>P/S = 6 > poppy oil, not heat-bodied (diFA C8/C9 = 4.6).<br>**FTIR:**<br>Oil, lead white and lead carboxylate. | Lead white paint in poppy oil, not heat-bodied. |
| CL8<br>Brown border line that separates two scenes. | No analysis done. | **Py-TMAH-GCMS:**<br>P/S = 2.8 ‡ nut oil, slightly heat-bodied (diFA C8/C9=5).<br>**FTIR:**<br>Oil, bone black and lead carboxylate. | Bone black in nut oil, slightly heat-bodied. |

Burmester and Denk found cobalt blue and Schweinfurt green in Corot's *Vue prise à Riva*, dated 1835.[53] By then, the pigment was easily obtainable and much used, despite its poisonous character. Few technical analyses have been performed on Corot's early works and therefore an earlier occurrence cannot be excluded. We may thus have an early indication for the use of Schweinfurt green in French painting shortly after 1822, the year when the sulfate method of preparation was made public in France.
In the cross-sections of the greens in the centre landscape (CL2-3) however, no arsenic is present in the green pigment particles, which excludes the use of Schweinfurt green. XRD results show the presence of pseudo-malachite (copper phosphate hydroxide) in the dark green layer (CL3).[54] It is unlikely though that all the green particles consist of pseudo-malachite, since no phosphorus was identified in the green particles by SEM-EDX, which indicates the presence of another copper based green.
The use of copperferrocyanide red in the top layer in the background of the girl also needs further comment. A variation of the pigment called Prussian brown described by Bouvier was mentioned by Standage in 1886 as 'the ferrocyanide of copper'. Also Church mentioned this variation and remarked in 1901 that 'this pigment contains a considerable quantity of a soluble salt of potash.'[55] The compound may be the same as the 'hydrocyanate of copper' which was mentioned by Hatchett in 1845,[56] the name of which bears resemblance to 'Hatchessbraun', one of the names for a ferrocyanide of copper mentioned by Kittel.[57] This rare pigment, which we prefer to call Florentine brown, may have been used for the reddish brown background next to the girl. This would account for the presence of iron and copper. We also indicated potassium, which may be explained as a residue from the manufacturing process. It is uncertain when the pigment became available.[58]
In the layers containing lead white, barium sulphate was found. The latter was used from the end of the 18th century as an addition to lead white paint. It was mixed in a variety of proportions: 'Venice white' 1 lead white: 1 barium sulphate, 'Hamburg white' 1:2, 'Dutch white' 1:3.[59]

· *Binding media*

Four organic analyses were carried out to establish Corot's use of binding media in his 'pre-tube' sketches (CL/4/6-8, see Table 1). Interestingly, the analyses demonstrated the use of poppy and/or walnut oils, not or slightly heat-bodied without further additives such as waxes or resins. The use of a slightly heated walnut oil or mixtures of oils, possibly linseed, was found in two layers in the cross-section (CL4) of the accumulated paints in the edge of the lid and in the dark brushstroke outlining the sketches.

White examined three early paintings by Corot dated between 1826 and 1836 using GC-MS and FTIR. In *The Roman Campagna with the Claudian Aqueduct* (1826, National Gallery, London), the only one of the three examined which is on paper mounted on canvas, he found heat-bodied linseed/walnut oil in the blue sky with a little pine resin, and heat-bodied linseed oil in the green area with a trace of pine resin and mastic resin. In the two paintings from the 1830s only heat-bodied walnut oil was found.[60] The latter two are on canvas and were probably executed in the studio.
Koller and Baumer found the frequent use of mixtures of various oils typical of French 19th century painting. The relatively slow drying poppy oil was, for example, often mixed with a quick drying linseed oil, *huile grasse* (linseed oil heat-bodied with a lead drier), to shorten drying times. The amount of *huile grasse* added depended on the drying properties of the pigments used.[61] They analysed works by Daubigny (four works, 1854-1876), Courbet (two works, 1854-1865) and Corot (two works, 1850-1860). In the two Corot paintings walnut, poppy and linseed oil were found in the paint layers as well as the use of a linseed oil varnish (*huile grasse*) rubbed on the paint surface. In the brown transparent layers they also found shellac soap and turpentine.[62] Their findings show that artists like Daubigny used binding media in complex combinations, while others like Courbet and Corot used a simpler system with a limited range of binding media.[63] Most Barbizon painters moved between these two extremes. The addition of driers to tube paints as well as heat-bodied drying oils can be considered as chemical improvements of the second half of the 19th century.[64]
The binding media used in our sketches seem quite straightforward: walnut and poppy oils, not or slightly heat-bodied, and in the sample from the inner edge of the lid: slightly heat-bodied, possibly mixed. The relatively high P/S ratio of 2.8 for the brown paint (CL8), which was used in the dark frame around the sketches, may be explained by walnut oil or, for example, a mixture of linseed and poppy oils. The lack of added drying oils, like *huile grasse*, is remarkable, as one would expect paints for outdoor use to need quick drying properties.[65]
If our dating of the sketches is correct these paints were, as said above and, unlike most of the paintings examined by White, Koller and Baumer, 'pre tube'. Possibly, looking at the complex pigment mixtures, they were made *in situ* by mixing oils with dry powder pigments on the palette, or they may have been prepared just before leaving for the countryside.



## Maris, Corot, 19th century paint tubes and brushes

· *Introduction*

At present the box contains fifteen tubes or remains of tubes, from various English, French and German colourmen: Lechertier, Roberson, Winsor & Newton and Newman, all based in London; Frères (or Ange?) Ottoz and Lefranc, both from Paris; plus Dr. Schoenfeld, a German paint manufacturer.[66] Some colour names can be clearly read: Terra Verde, Purple Madder, Lichter Ocker, Steinocker, and Light Red, others are indecipherable (fig. 21a-c). Dating the tubes is difficult. If we look at the addresses on the labels we can give a time span in which these tubes could have been bought from 1840, the date of the introduction of the collapsible metal tube, up till the late 1880s, the last date for the Winsor & Newton tubes.[67] Some of the paints analysed were introduced in the 1850s and 60s. From these dates, and the fact that most come from English colourmen, it seems that their most likely owner was Maris, with the possible exception of the French tubes from Alexis Ottoz and Lefranc, which may be dated before 1876 and 1880 respectively.

· *Tubes, technical analyses*

To identify the composition of the paints we performed PLM, SEM-EDX, DTMS, Py-TMAH-GCMS, and FTIR analyses on ten of the fifteen tubes, numbered T1-10. The results are listed in Table 2, for methods used see Table 3. We will discuss some of the results in more depth using the numbers of the tubes as direct reference to Table 2.

· *Binding media, additives, pigments*

Reviewing the analytical results we can say that a variety of oils was used: linseed, walnut and poppy oil, some heat bodied. The substance of poppy oil gave the prepared paint a buttery character, ideal for the paint handling demands at that time with its thick *impasto* and visible brush strokes.[68] Both walnut and poppyseed oil were especially suitable for lighter colours and for the *peinture blonde* as they yellowed less than linseed oil. Linseed oil, a quicker dryer, was used in particular in ground layers, or mixtures with the slower drying poppy and walnut oils.[69] Both Roberson's Purple Madder (T2) and Lechertier's Terra Verde (T1) and the ocherous paint from Ottoz (T8), seem to have some addition of an a non-drying (possibly rapeseed) oil. This is not uncommon. In 19th century documentary sources hempseed, cottonseed, and grapeseed oil and olive oil are mentioned as an addition to slow down the drying time of linseed oil.[70] Presumably the non-drying oil was added to improve storage properties of the paints in the tubes, or to slow the

fig. 21 a-c
**a**) Purple Madder, Roberson (T2)
**b**) Steinocker, ochre de ru, Dr. Schoenfeld (T7)
**c**) Ottoz, red and orange ochre containing tube (T8)

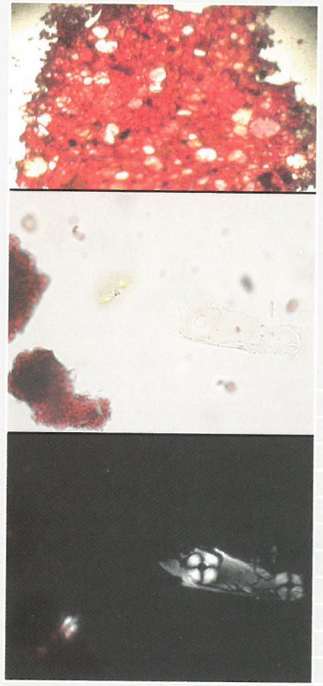

fig. 22 a-c
Microscopy images of the red paint from Richard Aines (T5).
**a**) Sample squeezed in the Diamond Anvil Cell in the FTIR microscope. The transparent round particles are identified as starch grains. Red lumps correspond to red lake pigments.
**b**) Sample prepared for PL.
**c**) Idem, but in crossed polars. The characteristic cross for starch grains becomes visible

**Table 2.** Results of analyses of the tube paints

| Sample #, label, characteristics | PLM[1] | SEM-EDX[1] | DTMS[1,2] | Py-TMAH-GCMS[1,2] | FTIR[1] | Conclusions |
|---|---|---|---|---|---|---|
| T 1<br>Terra verde<br>Lechertier<br>Very soft green paint.<br>Some oil medium has run out from the paint. | Green, anisotropic partiicles, partly round, partly elongated; colours vary between yellow/green and blue/green > green earth. Some yellow and red anisotropic particles and brown, isotropic particles > ochres or umber. | Overall and in separate particles: Si, K, Fe, (Mg), (Al) | P/S= 1.2 > linseed oil. Some triglycerides still present. | P/S= 1.6 > linseed oil, not or slightly heat-bodied (diFA C8/C9 = < 1/6). Relatively high FA 22:1 and FA 20:1 contents > addition of oil (rapeseed oil?) | Absorptions identical with those in agreen earth reference spectrum, oil. The medium separated out of the paint: oil | Green earth in linseed oil paint. Possibly some addition of an oil such as (non-drying) rapeseed oil. Note: the ochres are most probably just a natural part of green earth and are no addition.[3] |
| T 2<br>Purple madder<br>ROBERSON & Co<br>Brittle, dark purple paint. | Isotropic, dark red particles, > red lake. Very fine red and yellow (partly anisotropic) > ochres. Also some very fine blue particles (ø 1 μm). | Overall: Al, S, Fe, (Si), (Ca) | Oxidised paint, with P/S= 1.4 > linseed oil.<br>Traces of lead. | P/S= 1.7 ‡ linseed oil, not heat-bodied (diFA C8/C9 = < 1/6). Relatively high FA 22:1 content ‡ addition of oil (rapeseed oil?). | Oil, inorganic hydroxide (aluminium hydroxide would be in accordance with the PLM and EDX findings). | An organic lake pigment on alumina in a linseed oil medium. Possibly some (non-drying) rapeseed oil present. Very fine red and yellow ochre (possibly intentional or unintentional contaminant of the red lake). A few unidentified blue particles, possibly French ultramarine.The lead identified by DTMS suggests the presence of a lead dryer. |
| T 3<br>Lichter Ocker / Ocre Jaune<br>Dr. Schoenfeld<br>Not completely dried brittle yellow ochre paint. | Partly anisotropic, partly isotropic very fine, yellow particles (ø < 1 μm) and some red particles > ochre and zinc yellow. Some angular transparent anisotropic particles > quarts. Few anisotropic needles > chrome yellow? | Overall: Al, Si, K, Cr, Fe, (S), (Zn), (Ca), (P), (Pb)<br>Particle: Si, Al, (Fe), (K), (Cr)<br>Particle: Si (only a few of these particles present) | Relatively oxidised paint, low amounts of unsaturated FA's / triglycerides. Zinc and lead present. P/S ratio = 3, which could relate to walnut oil. Additions of beeswax. | Oil and beeswax. DiFA C8/C9 > 1/8; P/S 4.8. The nature of the oil cannot be distinguished because of the beeswax content. | Oil. Silicates, similar to the reference spectra of Silicium/ Aluminium oxides. Yet unidentified additions (probably present in the oily medium; see T4) | A mixture of predominantly zinc yellow and yellow ochre (ø < 1 μm) in possibly nut oil paint. Beeswax is present. A few particles of red ochre and quarts and presumably very little chrome yellow. |
| T 4<br>Roman...?<br>Winsor & Newton<br>Very soft yellow ochre paint. Some oil medium has separated out. | Round isotropic yellow particles (ø max. 10 μm) > ochre. Fine, anisotropic, yellow needles > chrome yellow. Some orange-red isotropic (or little anisotropic) particles > ochre. Few anisotropic, angular, transparent particles > quarts. | Overall: Fe, Si, (Al), (Pb), (Sn), (K), (Ca), (Cr) Needle: Pb, Cr<br>Particle: Fe, Si, (Sn), (Ca), (Cr), (Pb).<br>Particle: Fe, Si, (Pb), (Sn), (Cr). (Ratio Fe/Si variable) | Fresh oil paint; many unsaturated fatty acids, triglycerides still present. P/S = 2.6 > nut oil. Lead. | P/S = 5.3 > poppy oil, not heat-bodied (diFA C8/C9 > 1/8). | Oil, iron oxides, indicating ochres. Unidentified additions in the separated medium (same as in T3). | Mixture of predominantly chrome yellow and yellow ochre in probably a poppyseed oil containing paint. A few particles of red ochre and quarts (probably component of yellow ochre?). |
| T 5<br>Richard Aines<br>Dried powdery reddish paint. | Dark red, isotropic particles, > organic red lake. Fine (1 μm), red, yellow and brown particles; some red particles are anisotropic > ochre. Transparent, anisotropic particles, showing a black cross when viewed in crossed polars > starch4.(See Fig. 22 | Particle: Fe, Si.<br>Particle: Al, Sn (low signal).<br>Several particles: Sn. Particle: Pb, Cr. Particle: Hg, S | Still large amounts of unsaturated fatty acids / triglycerides. P/S ratio = 2.0 > walnut oil. Clear presence of polysaccharides confirms starch grains observed by PLM. | P/S= 3.2 > walnut oil, slightly heat-bodied (diFA C8/C9 = 1/5). Some indication of an organic, bromine containing compound. | White grains are polysaccharides (see Fig. 22 PAS op! KJ). | Red organic (at least partly natural as identified with HPLC) lake on a possibly Sn containing substrate in walnut oil. Starch was probably used as an extender.[5] Traces of fine ochre, chrome yellow and vermilion also present. |
| T 6<br>Lechertier (?)<br>Half-dried, red-brown paint. | Orange-red, predominantly anisotropic, particles (ø 1-6 μm) > ochre. Transparent, anisotropic particles (ø max. 30 μm) > quarts. | Overall: Fe, Si, (Al), (Sn), (Ca), (Mn) | Not very oxidised. P/S ratio is 1.5 > linseed oil. | P/S ratio of 2.5 > walnut or mixture of oils. No indication for additives. Oil is not or slightly heat-bodied (C8/C9 diacid ratio = 1/6) | | Ochre containing linseed or walnut oil paint, not or slightly heat-bodied. Identification of manganese suggests that umber is present (alternatively a manganese-dryer). |
| T 7<br>Steinocker /Ocre de rue<br>Dr. Schoenfeld.<br>Very rubbery, soft ocherous transparent paint. | Red / red-brown, anisotropic particles; yellow, predominantly isotropic, particles (ø 10 μm) > ochre. Transparent, anisotropic particles show many interference colours (ø max. 30 μm) > calcite. Transparent, anisotropic particles > quarts. | Overall: Si, Fe, Al, (Pb), (Ca), (K), (Sn), (Mn), (Zn)<br>Several particles: Fe | No analysis done | P/S ratio = 5 > poppyseed oil. Unusually high amount of diacids. Slighthly heat-bodied oil (C8/C9 diacid ratio = 5) | Oil and iron oxide. | The paint contains yellow and red ochres, quartz and presumably umber in poppyseed oil, slightly heat-bodied. Calcite was probably used as a filler. The find of lead suggests the presence of a lead dryer in the paint. |
| T 8<br>Richard Aines<br>Etiket: ... de Lorette Toz fa (Alexis Ottoz?) Possibly it concerns a Light Red like or one of the Mars colours. | Anisotropic, round red and orange particles (ø 10 μm) > ochre. Several transparent, anisotropic particles show many interference colours (ø max. 30 μm) > calcite.<br>Some brown, isotropic particles. | Overall: Si, K, Ca, Fe, (Mg), (Al), (Sn), (Ti) | Relatively oxidised paint, still some triglycerides present from the oil medium. P/S ratio 1.1 > linseed oil medium. | P/S= 1.5 > linseed oil, not heat-bodied (diFA C8/C9 = < 1/7). Relatively high FA 22:1 content > addition of oil (rapeseed oil?) | | Mainly red and orange ochre containing linseed oil paint. Possibly some non-drying (rapeseed) oil added. Calcite was used as filler. |
| T 9<br>... DE ... Foncé (Jaune de Cadmium Foncé?) Top: Richard Aines Paris Shoulder: anchor, Lefranc Soft orange paint. | Very fine, little anisotropic, orange pigment. | Overall Cd, S | P/S 2 to 3 > walnut oil. Beeswax. Cadmium and (inorganic) sulphate or sulphide. | P/S ratio = 1.8 > linseed oil. Not heat bodied oil (C8/C9 diacid ratio = 7) | | Cadmium orange in probably linseed oil medium. The paint contains some beeswax. |
| T10<br>Light red<br>Winsor & Newton<br>Soft red paint. | Very fine (ø < 1μm), anisotropic, red particles ‡ ochre. Transparent, anisotropic particles ‡ quarts. | Overall (light area in BEI5): Si, Al, Fe, (K), (Ca), (Ti), (Sn) | Relatively dry oil, P/S < 2 > linseed oil. | Strongly heat-bodied linseed oil (P/S ratio = 1.6, C8/C9 diacid ratio = 3). | | A red ochre containing strongly heat-bodied linseed oil paint. |

drying. It might also be an adulteration of the linseed oil, perhaps even unknown to the manufacturer of the paint. We also found additions of beeswax (T3, T9), which was added as a suspension agent for the pigment to keep the oil from running, but also to improve the working properties of a paint with a relatively large proportion of oil to pigment. Vibert (1893) complains about the carelessness of colourmen who use too much oil: '...oil is cheaper than pigment, and the more there is of one, the less there need to be of another. Only the colours are so overloaded with oil at present that they run on the palette if wax is not added to restore some body to them...'.[71]

Although extenders were quite popular as cheap additions to oil paints, we have found relatively little evidence for them in the ten paints studied here. Small amounts of calcium, sometimes as yet unidentified particles (in T2-4, T6-8, T10) and quartz particles (in T3, T4, T6-7, T10) derive probably from the earth pigments in the mixtures. Thus the only real extender encountered is starch, indicated by FTIR (Richard Aines, T5), in a red lake containing paint. Starch seems to have been used relatively often as an addition to red lake paints (fig. 22a-c).[72]

We found some indications for added dryers. T6 showed manganese (from umber) and T2, T3 and T7 showed lead. T2 and T3 have no lead containing pigments thus here we can be sure the lead derives from a lead based dryer.

Small amounts of tin are present in five of the ten paint samples. In one case (T5) tin-containing particles were found which could be related to the substrate of the red lake. Otherwise we assume that some tin from the material of the tubes may have dissolved into the paint.

Most paints studied here turn out to be relatively straightforward one-pigment paints, yet at least four paint tubes (T2, T4, T5) contain mixtures of various pigments. This corresponds with the results from Townsend et al. (1995) who found a variety of mixtures, additives, and composed substitutes for traditional pigments or for 'new' hues, within singular tubes.[73] To decide whether pigments mixtures found in 19th century paint samples – especially from the post tube era, that is after 1840 – were made by the artists or came ready-made from the colourman, is rather tricky. We tested one of the two Roberson tubes both labelled 'Purple Madder' (T2). Several formulae for Purple madder can be found in Roberson's recipe books. The first is dated 1841 and contains Pink madder, French Ultramarine and Van Dyke brown – the latter term was crossed out by the manufacturer and replaced with Cappah brown, a bituminous earth pigment.[74] The second recipe, dated c.1864-66, contains Brown Madder, Pink Madder and French ultramarine.[75] From research on 19th century pigments, based on colour books from Winsor & Newton (1900) and Roberson (1880), as well as tube paints on palettes of James McNeill Whistler, it appears that Purple Madder, traditionally made from pure Madder, was substituted by a mixture of Pink and sometimes Brown madder and artificial ultramarine. Adulterations were plentiful. Townsend et al. found, among others, red and yellow ochres.[76] This seems to correspond quite well with our findings (See Table 2, T2).

HPLC analysis showed the presence of purpurin and alizarin, typical for madder; PLM indicated French ultramarine.[77] Van Dyke brown (or Cappah brown), mentioned in the Roberson recipe, was not mentioned elsewhere nor was it found in our analysis.

The name of the colour on the first Winsor & Newton tube (T4) is not wholly readable but appears as 'Roman..?' Comparing this with available Winsor & Newton tube paints, this could be Roman ochre, or burnt Roman ochre.[78] Its implied Italian origin seems to have indicated dark, reddish yellow hues of the earth pigment. We found, however, both yellow ochre and a small amount of chrome yellow in not heat-bodied poppy oil.[79] Chrome yellow had been commercially produced from 1818 and was criticized as being non-permanent, too bright, changing when mixed with organic pigments and so on. Despite this, chrome yellow appears in the catalogues of Winsor & Newton, Rowney and Reeves.[80] Lead chromate yellow as well as chrome orange and red were quite popular among artists.[81] For example, in Constable's paint box (1837), the yellow pigment used in two of three bladders with yellow paint is lead chromate yellow.[82] It was also identified in various paintings by Honoré Daumier.[83] It may have been added to the yellow ochre in our tube to intensify the yellow hue. Interestingly Merimée observes: '...it is not however, a permanent colour...in a few years its brightness goes off like yellow ochre...'.[84]

The other Winsor & Newton tube is labelled Light Red (T10). Winsor & Newman disclosed in 1896 that this was made by calcining yellow ochre. Our analysis showed that the paint consists in fact of red ochre in a strongly heat-bodied linseed oil, which was used to improve the working properties of this relatively medium rich paint and decrease drying times.[85]

The French tube from Lefranc (T9) has a badly damaged label on which the words '... de ... Foncé' can be read. The analysis showed that the tube contains only Cadmium orange, a pigment that was introduced to the market in the early 1860s. It appears in the catalogues of Winsor & Newman in 1864.[86] Presumably Lefranc introduced it at much the same time. The name therefore may be *Jaune de Cadmium Foncé*, and the tube should be dated after 1860 and possibly before 1880, when the company introduced

another symbol on the label, tops and shoulders of their tubes. As a binding medium we found linseed oil with beeswax as an additive.
The analysis of the tube with the label[87] *Steinocker/Ocre de rue* or *ru*, showed that the paint contains yellow and red ochres, and also quartz, some umber and calcite – all probably naturally present – in a slightly heat-bodied poppy oil (T7). The presence of lead may indicate the use of a lead drier. *Ocre de rue* or *ru* is a French name similar to the English *oker de rouse* used in 17th century sources for a reddish or brownish yellow ochre.[88] The mixtures of yellow and red ochres, and presumably some umber, confirms the apparently characteristic reddish brown hue of the colour.
The other tube with a similar style label contains *Lichter Ocker/Ocre Jaune* (T3). Here analysis indicated both zinc yellow and yellow ochre as the main pigments present. Chrome yellow, and a little red ochre and quartz were also found. The binding medium is possibly walnut oil with addition of beeswax. Zinc yellow or Citron yellow, a chromate of zinc and potassium was sold as an artist's colour from the 1850s. Winsor & Newton list it in 1861.[89] T7 contains poppy oil, and T3 walnut oil (or a mixture of poppy and linseed oils), slightly heat-bodied.

- *Brushes*

The box contains eight brushes, the hairs held together in metal ferrules. Six are marked Newman, 24 Soho Square, two are anonymous. Unusually the ferrules are bent backwards and the hairs are cut short. Painters' manuals often advise against the cutting of brush hair; cutting removes the natural points of the animal hairs, and the short stiff hairs leave marks in the paint.[90] Using these brushes would rub the paint from the canvas rather than apply it to it. Thomson describes Maris using dry rags and even little sticks to rub and scratch the paint.[91] It is easy to visualise how Maris could have achieved the nebulous appearance of his later works with these modified brushes; abraded areas with the canvas structure clearly visible play a vital part in the total effect. But further research on Maris' techniques has yet to be undertaken and we therefore lack conclusive evidence. On the 1923 photograph of the Maris-memorial room, the painting box contains several brushes. The English make, modern concept and manipulated form all point to Maris as their user.

## Conclusion

This study provided evidence on the provenance of the Corot painting box, showing that Maris owned it after 1875, and probably used it in his London studio to store his materials. The study also supports the proposition that Corot actually painted the sketches in the lid during his first visits to Normandy and Italy in the 1820s. The box was intensively used, as we would expect from our knowledge of Corot's active early years as a painter: following the advice of his masters Michallon and Bertin to paint frequently outdoors. The fact that many of his early works on paper have measurements corresponding with the inside lid of our painting box, confirms its possible use in those years.
The cross-sections taken from the sketches presented interesting information about Corot's early practice as a landscapist. In the sketches some relatively new pigments like cobalt and Schweinfurt green were found. Although Schweinfurt green was invented in the beginning of the 19th century, the date of its first use is still unknown. Also the early use of Florentine red as well as baryte has so far not been documented extensively in the literature. However, the use of Schweinfurt green in combination with the evidence that the sketches were painted somewhere between 1822 and 1830 seems to indicate hat Corot must have used this pigment relatively soon after its invention, maybe obtaining it from a German colleague. Interestingly the sulfate preparation method of Schweinfurt green was published in France in 1822. There is a simple use of binding media in the sketches and complex mixtures of pigments. Possibly Corot mixed the paints *in situ* or used paint from bladders prepared according to his demands.
The content of the box dates from after 1840. As could be expected we did not find any technical link between the tubes and the paints used for the sketches. The paint tubes and brushes presumably belonged, with two possible exceptions, to Matthijs Maris. Analyses showed mixtures of pigments, heat-bodied oils, the use of additives like beeswax, a non drying oil, and most interestingly starch used as an extender.
Finally, the study confirms our belief that this type of object can provide fresh and compelling insights into a painter's methods and materials; and in this instance also into the painter's travel experience.



**Table 3.** Methods & Techniques

Light microscopy
Light microscopy on paint cross-sections gives information of the layer build-dup, as well as limited information on the pigments and binding media. Samples were embedded in polyester resin and after grinding with SiC-paper examined under a Zeiss Axioplan 2 microscope. Incident normal and UV-light (Xenon lamp and high-pressure mercury vapour lamp, respectively). Filter set 'UV H365': excitation BP 365/12, beam splitter FT 395, emission LP 397.

PLM
Polarised Light Microscopy gives information on separate pigment particles from a paint sample. In case of the tube paints samples, pigment grains were separated from the medium by dissolution of the medium in morpholine, mounted in Permount histological medium (n = 1.539) and examined in polarised light.

SEM-EDX
Scanning Electron Microscope-Energy-Dispersive X-ray spectroscopy tells us about the elemental composition of pigments in paint cross-sections. Analyses were performed at Shell Research and Technology Centre, Amsterdam, using a JEOL JSM 5900 LV scanning electron microscope and a Noran Vantage EDX-system with pioneer Norvar detector. Electron beam 25 kV. Samples were coated with carbon before analysis. Some analyses were performed at ICN: As at SRTCA but with a JEOL JSM 5910 LV SEM, and electron beam 20 kV. No carbon coating.

FT-IR
Fourier Transform infrared analyses are performed for obtaining fingerprinting information of both organic and inorganic materials in mg samples. A Perkin Elmer Spectrum 1000 FTIR spectrometer combined with a Perkin Elmer AutoImage System FTIR Microscope, using a Miniature Diamond Anvil Cell with type IIa diamonds.

DTMS
Direct Temperature-Resolved Mass Spectrometry is used to obtain fingerprint information on compounds similar to FT-IR. Analyses were performed at the Institute of Atomic and Molecular Physics (AMOLF), Amsterdam. See for example K.J. van den Berg, J.J. Boon, I. Pastorova, L.M.F. Spetter, 'Mass spectrometric methodology for the analysis of highly oxidised diterpenoid acids in Old Master paintings', Journal of Mass Spectrometry, 35 (2000), 512-533.

Py-TMAH-GCMS
With Pyrolysis Gas Chomatography-Mass Spectrometry (with Tetramethyl Ammonium Hydroxide) specific information can be obtained from e.g. the nature of an oil, resin, or wax. See for example K.J. van den Berg, M. Geldof, S. de Groot and H. van Keulen. 'Darkening and surface degradation in 19th- and early 20th century paintings – an analytical study', in ICOM Committee for Conservation 13th Triennial Meeting, Rio de Janeiro, 22 -28 September 2002, 2002, in press.

XRD
X-Ray diffraction is used for the elucidation of crystalline materials (mostly anisotropic pigments). A sample of solid material, size 0.5 mm2 is attached on the tip of a glass fibre with a small amount of cedar oil. X-ray camera: Debeye – Scherrer powder camera; 2r = 57,3 mm. Philips PW 1024. X-ray generator: Philips PW 1830. X-ray film: double coated CEA REFLEX 25. Exposure conditions: Kv 40, mA 30, time 300 min., Copper tube.

HPLC
High Performance Liquid Chromatography was performed for the analysis of organic colourants in lake pigments. The sample is hydrolysed by addition of 100 µl reagent (water/methanol/hydrochloric acid, 1/1/2) and heated for 10 min. at 100 °C to extract and dissolve the dyestuff. After hydrolysis, the sample is evaporated to dryness and dissolved in 25 µl dimethyl formamide. Analysis by gradient HPLC-PDA by injection of 10 µl sample. HPLC Column: Phenomenex luna C18-2, 3 µm (100 x 2 mm), Eluents: Buffer A: methanol:water (10:90, v/v), buffer B: methanol, buffer C: 5% w/v phosphoric acid in water, flow rate 0,2 µl/min. Total analysis time: 45 min. Detection: Waters PDA 996, 200 to 700 nm, 1 scan./sec.

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**Notes**
**1** Inv.no. MH 11_z.j.mb concerns items a t/m f: 'a. paint box on wheels/ b. brushes 12/ c. paint box (handwritten: *from Corot, bought by Matthijs Maris on the auction Corot*)/d. box for brushes / e. bed (*missing*)/f. 4 palettes (*one of A. Mauve; one with text: last palette of Jacob Maris 1899*). This documentation suggests that possessions of the Maris brothers arrived at the museum simultaneously. Auctioncatalogue: 26 mai- 9 juin - Paris - *Corot (Camille) peintre* Exp: Durand-Ruel, Mannheim. 931 Nos. Studio paraphernalia were not mentioned in the auction's catalogue. This is, however, not uncommon.
**2** A. Wagner, Matthijs Maris, [Exh. Cat. Haags Gemeentemuseum], (The Hague, 1974/75); J.F. Heybroek, 'Matthijs Maris in Parijs: 1869-1877', *Oud Holland*, 84 (1975), 266-289
**3** On Matthijs Maris see M. Haveman ed., 'Matthijs Maris, een vreemd bestaan', *Kunstschrift*, 1, (1990), this issue of Kunstschrift is devoted to Matthijs Maris, with bibliography (1898-1990).
**4** Letter dated 27 februari 1892, *Kunstschrift*, 1 (1990), 45-46.
**5** E. D. Fridlander, *Matthew Maris*, (London & Boston, 1921), 114-15.
**6** Fridlander 1921, 59.
**7** E.J. van Wisselingh supported Maris financially during his London sojourn to give him freedom of artistic expression without having to produce what Maris called 'potboilers'. Wisselingh dies in 1912. To show his appreciation Maris leaves all his possessions to Isabella van Wisselingh. See Wagner 1974/75, 24
**8** Communication from J.F. Heybrock. See: R.W.P. Jr., 'De Thijs Maris-kamer in de akademie te Amsterdam', *Geïllustreerde Elsevier*, 2 (1923), 67, fig. on page XIV.
**9** See note 1. The objects seem to have been inventoried shortly after the arrival of objects from Jacob Maris in 1921. The chairs and table on the photo are still in the museum collection, the four-poster bed is missing.
**10** J. Breton, *La Vie d'un Artiste: Art et Nature*, (Paris, 1890), 239.
**11** V. Pomarède, 'The Making of an Artist', in: G. Tinterow, M. Pantazzi, V. Pomarède, *Corot*, [Exh. Cat., Grand Palais Paris, National Gallery of Canada, Ottawa, Metropolitan Museum, New York], (Paris/New York, 1997), 12-14.
**12** Quoted and translated by Pomarède 1997, 16, from Corot, *carnet*, 1825, Musée du Louvre, Paris.
**13** M. Clarke, *Corot and the Art of Landscape Painting*, (London, 1991), 28.
**14** Pierre-Henri Valenciennes, *Éléments de perspective pratique à l'usage des artistes, suivis de réflexions et conseils a un élève sur la peinture et particulièrement sur le genre du paysage*, (Paris 1800), 404-419. There is a modern reprint, Geneva 1973.
**15** On his early Italian years see f.e.: Pomarède 1997, 17-28; Clarke 1991, 28-48.
**16** Pomarède 1997, 25.
**17** Valenciennes 1800, 404: 'des maquettes faites à la hâte, pour saisir la Nature sur le fait.'
**18** J. Bouvier, *Manual des jeunes artistes et amateurs en peinture*, (Paris, 1827), 542-3. Quoted by A. Callen, *The Art of Impressionism. Painting Technique & the Making of Modernity*, (New Haven & London, 2000), 26, her translation.
**19** Leslie Carlyle's personal communication: The sizing and priming of paper is mentioned in the Winsor & Newton archive: [69] 'Sketching Oil Paper. The paper is sised with/ the best patent sise/ made by Young's it is/ put on the paper with/ a large brush called/ a pound brush generally on the rough side/ when dry the following/ color is applied & stippled/ [..][on?] it is made the same/ as the finishing color/ of the Millboards only with a little ore/ Oil.' See also L. Carlyle, *The Artist's Assistant. Oil painting instruction manuals and handbooks in Britain 1800-1900 with references to selected eighteenth-century sources*, (London, 2001), 190. Callen 2000, 26-7, also mentions impregnation of the paper with oil.
**20** For example: *Bois-Guillaume, near Rouen: a gate flanked by two posts*, 1822, 24 x 32 cm, Galleria Internazionale

Arte Moderna, Ca'Pesaro, Venice;
arrières Saint Denis, 1823-24, 18 x 29 cm
ery similar in style with the small
ndscapes in the lid; *The Colosseum seen*
*rough the Arches of the Basilica of*
onstantine, 1825, 23 x 34 cm Louvre,
ris; *Rome: the convent of Sant'Onofrio,*
*the Janiculum*, 1826,
x 33 cm Fitzwilliam Museum,
ambridge; *Sky study*, 1826-28, 14.5 x
.5 cm, Collection of Claude Aubry,
ris, to name just a few. See also
Galassi, *Corot in Italy: Open-Air*
*inting and the Classical-Landscape*
*adition*, (New Haven, London, 1991),
-9.

**1** Callen 2000, 8.

**2** Corot makes two more trips to
aly. However, he seems to have not
sited Naples again as he travelled to
ome and stayed for longer period in
e north of Italy and Switzerland.

**3** V. Pomarède and G. de Wallens,
rot *extraordinary landscapes*, Gallimard
Réunion des Musées Nationaux, 51
r the illustration of this drawing.

**4** A. Robaut, *Corot, catalogue raisonné*
*illustre*, (Paris, 1965).Robaut 186, oil,
,2 x 41 cm, Louvre, Paris. See also
alassi 1991, 204-207.

**5** A.R. Murphy, *Visions of Vesuvius*,
luseum of fine Arts, (Boston, 1978), 5.

**5** Murphy 1978, 13.

**7** Valenciennes 1800, 225-226: ' ...ces
rrains offrent des sîtes variés, riches
pittoresques, dignes d'attirer l'atten-
on de l'Artiste, et d'exercer son pin-
au.'

**8** Valenciennes 1800, 278: 'L'eruption
un volcan est le spectacle le plus terri-
le et le plus magnifique que puisse
résenter la Nature'; and 279: 'Il est à
ésirer qu'un peintre puisse, une fois
ans sa vie, être témoin de l'Eruption
un volcan.'

**9** Valenciennes 1800, 276: 'Comme la
ouleur de ces laves, soit générale, soit
articulière, offre des tons entiers rou-
es, jaunes, bruns ou noirs, les mon-
ignes volcaniques ont toujours l'air
'être plus près qu'elles ne le sont
ffectivement. Cet effet est très sensib-
s à Naples ...'

**10** A drawing with a view on Capri
rvives: Robaut 1965, 2633 verso,
en and ink over pencil and paper,
x 31 cm, Louvre, Paris.

**11** An interesting painting from this
eriod shows a similar use of colour
nd a possible area of where the sketch
the lid could have been made: *Rouen*
*en from hills overlooking the city* (c.
329-1834), oil on canvas, 26,4 x 41,9 cm,
he Wadsworth Atheneum, Hartford,
he Ella Gallup Sumner and Mary
Catlin Sumner Collection Fund,
1931.187.

**12** Pomarède 1997, cat. 16, 56-57;
see also Galassi 1991, 144-145;
Valenciennes 1800, 400.

**13** Département des Arts Graphiques,
Musée du Louvre, Paris, A.R. 8 L 5.
See also Pomarède 1997, 20-21.

**14** Pomarède 1997, 20-21.

**15** E. Moreau-Nelaton, *Histoire de*
*Corot et de ses oeuvres*, (Paris, 1905), 18: 'Si
c'est oui, tu voudras bien aller chez
Colcomb-Bourgeois, quai de l'Ecole, au
Spectre-Solaire, près le Pont-Neuf, et
lui demander s'il a du jaune d'antimoi-
ne bien réussi. Si non, il n'en faut
pas.....Ainsi donc,
s'il est bien bon, tu en prendrais une
livre. (L'once coûte 2 francs). En plus
prends trois quarterons de jaune de
mars.'

**16** S. Constantin, 'The Barbizon pain-
ters: a guide to their suppliers', *Studies*
*in Conservation*, 46, I (2001),
49-67, 52.

**17** Constantin 2001, 57. On canvases
from 1850 up till 1873, stamps from
Ottoz, a family business were found:
Jérôme Ottoz (1850s), Ange Ottoz
(1860s), and Alexis Ottoz (1870s).

**18** A. Roy, 'Barbizon Painters:
Tradition and Innovation in Artists'
Materials', in *Barbizon. Malerei der*
*Natur-Natur der Malerei*, A. Burmester,
C. Heilmann, M.F. Zimmerman eds,
(Munich, 1999), 330-342, 333. Note
however that as an example the
painting *Avignon from the West*, dated
1836 is mentioned; with its measure-
ments, 33,7 x 73 cm, and painted on
canvas, this work is, although a
'sketch', in a different category than
the small open-air sketches in oil on
paper.

**19** See J. Leighton, '"Bienheureux les
paysagistes!" Landschaftsmalerei unter
freiem Himmel', in *Corot, Courbet und*
*die Maler von Barbizon*
*"Les amis de la nature"*, C. Heilmann,
M. Clarke, J. Sillevis eds., (Munich,
1996), 23-31.

**20** Quoted by Galassi 1991, 154, from
Corot's sketchbook , Louvre, Cabinet
des dessins, R.F. 6742 *bis*, Paris.

**21** See on the depiction of light and
Corot: Callen 2000, 86-8. Darkening
could happen with the dark medium
rich glazes used in the depiction of
*clair-obscure*.

**22** S. Cove, 'Mixing and mingling:
John Constable's oil paint mediums c.
1802-37, including the analysis of the
'Manton' paint box', in *Painting techni-*
*ques. History, Materials and*
*Studio Practice*, A. Roy, P. Smith eds.,
Preprints IIC Dublin Congress,
(London, 1998), 211-216, plates 96-97.
The paints in the bladders were analy-
sed to identify pigments, binding
media, additives, extenders, driers etc.

**23** P. L. Bouvier, Handboek voor de
jonge beoefenaar ....., (Breda 1830), 102.

**24** Bouvier 1830, 116.

**25** Gebr. Susse, *Volledige handleiding tot*
*de Teeken- en Schilderkunst, voor schilders*
*en liefhebbers*, (Amsterdam, 1845), 4: '
...while one, being in the countryside
or travelling, when one has the paints
in powder, it is easy to prepare them
oneself. For this purpose one needs a
palette and a glass muller, the paints
are tempered with poppy oil...' (our
translation). He also mentions the
availability of powder pigments as well
as paints in bladders.

**26** Carlyle 2001, 199.

**27** Carlyle 2001, 470-1.

**28** I. Fiedler, M. A. Bayard, 'Emerald
green and Scheele's green', in *Artists'*
*Pigments*, E. West FitzHugh ed., vol. 3,
(Washington/Oxford, 1997), 232-238;
there are two methods: the acetate and
the sulphate method. See for the first
description of the sulphate method H.
Braconnot, 'Sur une très-belle couleur
verte', *Annales de chimie*
*et de physique*, 21 (1822), 53-56.

**29** Fiedler and Bayard 1997,
219-271, 222.

**30** Fiedler and Bayard 1997, 223.

**31** J. H. Townsend, *Turner's painting*
*techniques*, [exh. cat. Tate Gallery]
(London, 1993), 39-48.

**32** Mentioned by D. Bomford, J. Kirby,
J. Leighton, A. Roy, *Art in the Making.*
*Impressionism*, (London, 1991), 58-9;
Carlyle 2001, 493-4.

**33** Oil on canvas, 98,6 x 141,5 cm,
Bayerische Staatsgemäldesammlungen
Munich. See: A. Burmester, C. Denk,
'Blue, Yellow and Green on the
Barbizon palette', *Zeitschrift für*
*Kunsttechnologie und Konservierung*, 13,
I (1999), 79-87, 84. More extensively in:
'Comment ils inventaient ces verts
chatoyants? Blau, Gelb, Grün und die
Landschaftsmalerei von Barbizon',
in: Burmester et al. 1997, 295-329.

**34** On pseudo-malachite see N.
Pisareva, 'A note on the use of blue and
green copper compounds in paintings',
*Studies in Conservation*, 39 (1994), 277-
283.

**35** Carlyle 2001, 488

**36** Carlyle 2001, 487

**37** H. Kittel, *Pigmente. Herstellung,*
*Eigenschaften, Anwendung*, (Stuttgart,
1960), 241: 'Wichtiger ist das
*Florentinerbraun*, Hatchess-, Neubraun
oder Van Dyckrot, ein Ferrozyankupfer,
$Cu_2Fe(CN)_6$. Man stellt es aus
Kupfersalz und Ferrozyankali her
(Hatchessbraun). Wird bei Gegenwart
von Ammoniak und Kreide gefällt,
so heibt es Van Dyckrot. Es ist sehr
verschieden im Ton, rotbraun bis
braunviolett, gegen Alkalien, Hitze
und Schwefelwassestof empfindlich
und für Kunstlerfarben nicht
genügend beständig, für andere
Zwecke aber zu Teuer.'

**38** See Carlyle 2001, 488; R. D. Harley,
*Artists' Pigments c. 1600-1835*, 2nd ed.
(1st ed. 1970), (London, 1982), 153.

**39** Carlyle 2001, 514, 516; R. J. Gettens,
G. L. Stout, *Painting Materials*, (New
York, 1966), 96; Harley, 1982, 174-176.

**40** R. White, J. Pilc, J. Kirby, 'Analyses
of Paint Media', *National Gallery*
*Technical Bulletin*, 19 (London, 1998), 74-
95, in particular 79-83, Table on 90-91.
*The Seine near Rouen*, 1830-5, oil on
canvas, and *Avignon from the west*, oil on
canvas, both National Gallery London.
Analysis of later works, 1855-1872,
where tube paints are most likely used,
shows mainly walnut oil, mostly heat
bodied, some heat bodied poppy oil,
some linseed oil partially heat-bodied,
and in some cases additions of pine
resin, beeswax, mastic resin and copal.

**41** Koller & Baumer 1997, 352.

**42** One should remember though that
these results concern later, (most likely
studio) works when tube paints were
widely available. See for more analyses
of binding media of the Barbizon
school: J. Koller, U. Baumer, 'Die
Bindemittel der Schule von Barbizon',
in Burmester et al. 1997, 343-369. The
linseed oil varnish may derive from a
conservation treatment and may not
have been applied by Corot himself.
Exclusion of this possibility is not
discussed. They describe the history
of the analytical methods used for the
identification of binding media as
well as problems and limitations, and
explain their own approach using
extraction, hydrolyses and derivation
processes to prepare samples, followed
by CC/MS analyses.

**43** Koller & Baumer 1997, 361- 366. In
general in the works they examined
poppy oil (sometimes heated), walnut
oil, *huile grasse*, and turpentine resins
in opaque paint layers; turpentine
resin, dammar and mastic in dark
paint layers; and beeswax, shellac soap
and bitumen as additives, were found.

**44** See Roy 1997, 336.

**45** White 1998, 79.

**46** 2 x Lechertier (London), 2 x
Roberson (London), 2 x Winsor &
Newton (London), 1 x Newman
(London), 3 x Richard Aines (Paris), 1
x Lefranc (Parijs), 2 x German ? make.

**47** We thank Sally Woodcock for the
information on the addresses of the
various English colourmen. See also
Carlyle 2001, 279. See on colour
merchants and the Ottoz firm:
Bomford et al. 1991, 41-3. Constantin
2001, 65, describes all the Ottoz
establishments from 1827-1885.
Roberson & Co: 1819 at 54 Long Acre,
London; 1853 - 1937 at 99 Long Acre.
Lechertier Barbe: 1827- c.1899 at 60
Quadrant Regent Street. Winsor
&Newton: 1832 at 38 Rathbone Place.
1886 they extended to 42 Rathbone
Place. Both tubes in the box are label-
led 38 Rathbone Place, placing the
date of production between 1841 and
1886, and possibly even thereafter
because the number 38 was still in
use then. The tube with ' ....de
Lorette', and '....toz Fr. (fa?)or A' on
the label appears to be from the firm
Ange Ottoz founded in 1827 in Paris.
His son Alexis Ottoz
started his establishment at the 47
Rue Notre-Dame-de-Lorette in 1862.
The shop closed in 1876, one year
after Corot's death. Lefranc was foun-
ded
in 1773 by Jean Laclef. From 1838 in
partnership with Alphonse and Jules
Lefranc the firm traded under the
name of Lefranc & Cie up till 1885.

**48** Callen 2000, 100-1.

**49** Bomford et al. 1991, 72-5.
Analyses of paint samples from
French impressionist painting dated
between 1862-1886, show a clear pre-
ference for poppy and walnut oil,
some linseed oil,
some linseed and poppy oil mixtures.
Linseed oil was predominantly the oil
used in ground layers.

**50** See on the various oils used in
19th century paints, treatises, colour-
men's catalogues etc.: Carlyle 2001,
23-9.

**51** J-G. Vibert, *La Science de la*
*peinture*, (Paris, 1893) (10th ed.), 116.
Quoted by Callen 2000, 100 (her trans-
lation).

**52** We found starch grains in a red
lake on a painting by Renoir:
A. Burnstock et al., manuscript on
materials' use and painting techni-
ques in four Renoir paintings in the
Courtauld Institute of Art, London,
in preparation. The starch additives
were also found in various instances
in analyses of red lakes and other
paints from 19th Century paintings
in the collection of the National
Gallery in London (Catherine Higgit,
National Gallery, personal communi-
cation).

**53** See Table 1-4 in: J.H. Townsend,
L. Carlyle, N. Khandekar, S.
Woodcock, 'Later nineteenth century
pigments: evidence for additions and
substitutions', *The Conservator*, 19
(1995), 65-77.

**54** Cappah brown was an earth
pigment from a mine newly opened
in 1814. See Carlyle 2001, 485.

**55** Carlyle 2001, 501.

**56** Townsend et al. 1995, Table I, 67,
Table 4, 69. On Whistler: J. H.
Townsend, unpublished report,
Hunterian Art Gallery, Glasgow.

**57** M. van Bommel (ICN) performed
the HPLC analysis. He found 85%
purpurin and 15% alizarin. Similar
amounts were found in madder con-
taining paints in paintings by Van
Gogh. However, normally the opposi-
te ratio is found. This may depend on
the
processing methods. Also terms like
Pink Madder, Brown madder in
colourmen's books, probably repre-
senting
a certain hue, need investigation
(comment M. van Bommel).
Further research on this matter will
be performed by Van Bommel and
colleagues (ICN).

**58** See Carlyle 2001, Tables 5-7.
Roman Ochre was listed with the yel-
lows and available from 1835, or
listed among the browns and availa-
ble from 1852 -,
– or Burnt Roman Ochre – available
from 1849 categorised among the
reds, or 1856, categorised among the
browns.

**59** Harley 1982, 89-90, describes the
discovery of chromium by Vauquelin
and its commercial production by
Bollman. See also Gettens & Stout
1966, 106-7.

**60** Carlyle 2001, 521.

**61** See Bomford et al. 1991, for a full
description of the development of the
pigments and their use.

**62** Cove 1998, Table 1, 211.

**63** A. Burnstock, W. Bradford, 'An
examination of the relationship
between the materials and techni-
ques used for works on paper, canvas
and panel by Honoré Daumier', in
A. Roy, P. Smith 1998, 217-222, Table
1, 218-9 and, 221.

**64** Quoted by Carlyle 2001, 521,
from: J.F.L. Mermimée, *The Art of*
*Painting in Oil*, (1830), English transl.
1839, 94-6.

**65** Strongly heat-bodied oils can
be associated with copal-oil media,
which were popular in the 19th
Century. We did not find any
indication for the presence of this
resin/oil medium. K.J. van den Berg,
J. Ossebaar and H. van Keulen,
'Analysis of copal resins in 19th
century oil paints and resin/oil
varnishes', *Art 2002*, in P. Van
Grieken, K. Janssens, L. Van 't Dack,
and G. Meersman eds., University
of Antwerp, (Antwerp, 2002).

**66** See Carlyle 2001, 500.

**67** Dr. Schoenfeld tubes are also
present among tubes belonging to
Matthijs Maris brother Jacob (collec-
tion Gemeentemuseum, The Hague).
Schoenfeld tubes were also imported
to London by Cornelissen & sons.
Various 'London' Schoenfeld tubes
are present in the collection of
Whistler's painting materials
(Hunterian Art Gallery, Glasgow).

**68** Norgate lists it among the
browns, and mentions that old Mr.
Hilyard [Nicholas Hilliard] used *Oker*
*de rouse* instead of English Ochre, to
shadow his flesh colours. See E.
Norgate, *Miniatura or the art of*
*limning*, J. Muller & J. Murrell eds.
(New Haven/London, 1997), extract
33, 245; and extract 36, 248.

**69** Gettens & Stout 1966, 178; Carlyle
2001, 523; Bomford et al. 1991, 63.

**70** Bouvier 1830, p. 175: ' A brush
...should never be trimmed with
scissors or otherwise. It should
always be a fine flower of hairs,
which because of their natural
conelike shape, make a point; as only
one or two cut down hairs already
make traces in the paint.' (our transl.)

**71** D. Croal Thomson, *Matthijs*
*Maris: An illustrated Souvenir*, (London,
1917), 24.

**Notes table 1**

1) See 'Table 3 Methods and
Techniques' for experimental details.
2) Elements in bold: abundant;
elements (between brackets): trace.
Sequence of layers starts with first
applied layer.
3) ‡ is 'indicating', 'suggesting'.
4) Conclusions on the type binding
medium are based on P/S values
derived by Py-TMAH-GCMS. The
extent of heat preparation of the oils
is derived from the C8/C9 diacid
ratios. In our experience, not-heat-
bodied fresh oils produce diacids
with a C8/C9 diacid ratio in the order
of 1/10, and strongly heat-bodied oil
with ratios up to 1/2.5. The latter oils
have been heated to more than 300 °C,
as is the case in e.g. the manufactu-
ring process copal-oil varnishes.
In this paper, 'slightly heat-bodied'
refers to ratios of 1/5-1/4.
5) The black particles may have been
formed in a reaction of Schweinfurt
or Scheele's green in layer 2 with
reactants in layer 3.
6) Copper sulphate was used in the
preparation of Schweinfurt green
via the sulphate process.
7) See text.
8) A very tiny sample was tested,
therefore we were not able to exclude
the presence of Prussian blue.
9) We were not able to identify the
blue copper pigment by XRD or PLM
despite its abundance in cross-
section.

**Notes table 2**

1) See also Table 1 and 'Table 3
Methods and Techniques' for
explanation and experimental details.
2) Conclusions on the type of binding
medium are based on P/S values
derived by Py-TMAH-GCMS and
DTMS. In case of deviation of the two
values, GCMS values are generally
considered more reliable. However,
since GCMS P/S ratios are affected by
additions of e.g. beeswax more than
in case of DTMS, DTMS values may
be preferred. See also Table 1.
3) Stefan Wülfert, Der Blick ins Bild,
(1999), 240: 'In grünen Erden werden
Glaukonit und Seladonit (K[(Al,
Fe(III)), (Fe(II), Mg)](AlSi$_3$,
Si$_4$)O$_{10}$(OH)$_2$) begleitet von weiteren
Silicaten sowie Eisenoxid/hydroxiden
und Calcit.'
4) Wülfert 1999, 211: 'Schliesslich
finden sich pflänzliche
Stärkekörnchen als Hilf- und
Verschnittstof zum Beispiel in
manchen Farblacken' and these
particles have a 'fast stehendes Kreuz'
when viewed between crossed polars.
See also text.
5) Backscattered Electron Image; a
light area indicates a narea of high
density with relatively heavy
elements

ADDITIONAL

PHOTO CREDITS

1, 3, 4-6, 9-11, 13-14, 21; Erma
Hermens/Astrid Kwakernaak;
2: Robaut, 136; 8,15-20, 22:
Netherlands Institute for Cultural
Heritage, Amsterdam.