Paintings in the laboratory: scientific examination for art history and conservation

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Flora & Pictura
‘the foliage tends almost to blue’

As early as 1734 the art collector Valerius Röver got rid of a painting by Jan Davidsz de Heem because ‘the colour had gone from some of the flowers’. Discolouration in paintings is thus not just a recent problem. Looking into the reasons for this phenomenon it appears that, lacking better materials, painters often worked with colorants that were not colourfast, such as smalt, Spanish green or verdigris and schietgeel. In addition to which, ‘restorers’ have often in the past caused irreparable damage, as a result of which the paintings can never again be seen in their original state.

In his Groot Schilderboek [Great Book of Painting] (c. 1690) Gerard de Lairesse says that to be a good flower painter one must be able to make an accurate drawing and have a thorough knowledge of perspective. He went on to observe that: ‘Further, one should have a good knowledge of the colorants, to know which are stable and permanent...’ from which it is evident that, at the end of the seventeenth century, the durability of the different pigments was known. Crispijn van de Passe describes in fine detail in his Den Blom-Hof of 1614 ‘how one can paint [flowers] in their own colours.’ The Hortus floridus is really a florilegium, a lavishly illustrated book on flowers, meant for garden lovers. Van de Passe was a copper-plate engraver. The illustrations in his book were not coloured in, although he mentions all the different colorants necessary for painting the flowers, stems, leaves etc. In contrast to De Lairesse, Van de Passe does not refer to the fact that several of the colorants mentioned by him were not light-fast. His

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1 This article is a revised and up-dated version of: Karin Groen, ‘het loof is wat na den blauwen treckende’, Kunstcrit, Openbaar Kunstbezit 3 (1987), pp. 106-111, that also appeared in: Ontrouw aan Rembrandt en andere verhalen, Amsterdam 1991, pp. 115-123.

2 Valerius Röver described his art collection in manuscript catalogues that are currently housed in the Amsterdam Universiteitsbibliotheek. The description of the paintings has been published. See: E. W. Moes, ‘Het Kunstkabinet van Valerius Röver te Delft’, Oud Holland 31(1913), pp. 4-24. See there on p. 20; an entry in Röver’s register dd. 1719 listed number 64: ‘een bloemstuk van Jan Davids de Heem, extra uitvoerig f 164.- gekogt op het boelhuijs van de kunstkoper Van Biesum te Rotterdam. Verkocht 1734 voor f 130.-, omdat de verf uit zommige bloemen was uitgetrocken.’

3 See: Truusje Goedings and Karin Groen, ‘Dutch pigment terminology II, ‘Schiet’ yellow or ‘schijt’ yellow?’, Hamilton Kerr Institute Bulletin Number 2 (1994), pp. 88-89, where it is shown that the name refers to the faecal hue of the pigment, although it is also prone to fading (verschieten – disappearing – yellow).

4 Gerard de Lairesse, Groot Schilderboek, Haarlem 1740, p. 357: ‘Nu zullen wy tot de zaak treden en aanmerken wat middelen ‘er zyn om een regten Bloemsschilder te worden; niet gelyk ze ons gemeenlyk voorkomen, maar gelyk ze behooren te wezen om den naam van Meester te verdienen. Doch voor af onderstellen wy, dat men daar onmogelyk toe kan geraaken zonder een vaste en nauwkeurige tekening, en een grondige kennis van de Perspectief. Verdiers dient ‘er een goede weetschap van de verwen by te wezen, te weeten die vast en bestendig zyn.’

5 Crispijn van de Passe, Den Blom-Hof, Utrecht 1614. Crispijn van de Passe, [Hortus floridus... A garden of flowers, Utrecht 1615.
engravings of flowers, if coloured in by hand later by the flower-lovers, either in water colour or
gouache, would be protected against the light. The instructions in the book would surely also
have been used by the flower painters - the artists who painted in oil.6

Apart from the use, either adjacent to or over each other, of materials that do not
tolerate each other, and apart from the natural ageing process, colours can also be affected over
the course of time by incompetent restorations.

Many paintings were subjected to such ‘restoration’ quite soon after their origin and in
some cases this is documented. In old manuals on painting techniques one often encounters
passages that deal with the cleaning and repair of paintings. Up to the eighteenth century, it was
the painters and owners of paintings who undertook such reparations. All too often they were not
sufficiently aware of the materials that had originally been used or of the effect that their
cleaning agents could have on these materials.

A few examples of these cleaning agents may be cited here. In a chapter of his book
Graphice (1658) titled ‘How to clean a grimy, or old oil painting’ William Sanderson
recommends that one use a sponge soaked in warm beer;7 while John Smith8 in 1676, advises
scouring the surface with water and smalt. Since smalt consists of finely ground particles of
glass, this must have had much the same effect as using present-day kitchen scouring agents.
Smith did add that this process should not be repeated too often because it would necessarily
remove some of the paint.9 His concern is evident from the fact that in the second edition of his
book, published in 1687 and re-titled The art of painting in oyl, and in subsequent editions, he
omits the use of smalt for cleaning pictures. Smith had probably copied the recommendation
from the much earlier The Excellency of the Pen and Pencil, by Albrecht Dürer (1471-1528).
Dürer’s manuscript text was printed in London in 1668. A recommendation for cleaning

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7 William Sanderson, Graphice: The use of the pen and pensil, or, the most excellent art of painting, in two parts,
London 1658, p. 86: ‘To make clean a foul, or old Picture in Oyle. Make clean the Picture with a spunge, dipt in
warm beer, and then let it dry; and afterwards wash it over with the liquor of the whitist Gum-dragon, steeped or
dissolved in water, which will set a glare or freshnesse upon the Picture. If you use blew starch, or glare of eggs, or
other such trash, as is very common, it will take off the heightning, and spoil the grace of the work.’

8 John Smith, The art of painting, London 1676, p. 74. ‘But if your Painting be more Curious, whether Figures of
Men, Beasts, Landskip, Frutage, Florage, or the like, then take Smalt, (a sandy Colour, to be bought at the Colour
Shops) with which and a spunge wet in water, let your Picture be gently scowred, and then cleanly washed off with
fair water: after it is well dry, let it be run over with Varnish, and you will find the beauty and lustre of your Picture
much recovered.’

9 Op. cit., note 8, p. 75. ‘too frequent operations in this kind must needs wear off a little of the Colours.’
paintings which regularly recurs is that of wood-ash in water; Dürer\textsuperscript{10} mentions it and Smith repeats it, with warnings. Smith was aware of the fact that this mixture - potash or potassium carbonate - corresponds to a strongly alkaline solution; not only are some colorants bleached but there is also the danger that the entire paint layer may be dissolved.

It is therefore hardly surprising that those who cleaned paintings came to realise, through bitter experience, that a less haphazard approach was necessary. Nevertheless, it was not until the end of the eighteenth century that the work of restoration was officially recognised as a trade in its own right.

The absence of a ‘good knowledge of pigments’ and the lack of stable paints have resulted in a great many changes in paintings. During investigation of Willem van Aelst’s \textit{Flower still-life with watch} in the Mauritshuis \textsuperscript{1} it appeared that it must have been the painter’s intention from the outset to render the leaves with at least a bluish green. This is inferred from the composition of the paint layers and the way they are built up in those parts of the leaves that are green, where a transparent green layer with verdigris was found above an opaque - natural ultramarine - blue.\textsuperscript{11} The transparent layer works as a glaze, which means that the underlying blue layer plays a role in the eventual colour effect. A century earlier a green glaze was mostly applied on a yellow green underlayer, consisting of a mixture

\textsuperscript{10} Albrecht Dürer, \textit{The Excellency of the Pen and Pencil}, London 1668, pp. 106-107. ‘Take your purest white Wood-ashes you can get, and sift them very well in a fine lawn sieve; or else some Smalt, which is as some call it Powder-blew, and with a fine Spunge and fair water wash the Picture you intend gently over, but be sure you have a great care of the Shadows, for by the ignorance of many persons many good Picture hath been abused...’

of a yellow and a green pigment. With Van Aelst, the blue underlayer was quite clearly not originally green; neither yellow pigments nor the discoloured remains of such could be found.

Two similar flower still lifes by Van Aelst (Ashmolean Museum, Oxford) [2] were also investigated. Parts of the foliage in the Oxford paintings are just as blue as the gentians, but with the microscope the remnants of green, brown-green and yellowish glazes are found everywhere. In some places, moreover, the paint layers are so thin and abraded that leaves can be seen through the overlapping flowers [3]. Although some paint layers become more transparent with time as a result of ageing, the current appearance of the leaves is more probably due to earlier cleanings.

In the seventeenth century painters had difficulty obtaining a grass-green colour. Samuel van Hoogstraten complained: ‘But I wished that we could also have green, like red or yellow, as we wanted it. Green earth (Terra verde) is too weak, and Spanish green is too harsh’. 

Indeed, in 1692 W. Beurs remarked in his De Groote Waereld in ’t klein geschildert that he would pass over green, since one could make it from blue and yellow. Similar pronouncements had already been

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12 Samuel van Hoogstraeten, Inleyding tot de hooge schoole der Schilderkonst: Anders de zichtbare Werelt. Rotterdam 1678. Derde Hoofdeel. Van de Verwen, p. 221: ‘De groene verwe verquikt de quaede oogen, zegt Seneka; maer ik wenschte wel, dat wy zoo wel het groen, als het Rood of Geel, tot onzeijn wil hadden. Terra verde is te zwak, en spaens groen te wreed, en d’assen t’onbestandig. Het berggroen is by ouden tijden tot het aensmeeren van kladderyen gebruikt geweest. ’tGroen beteykent jeugd, schoonheit, vreugd en onverdorvenheit, en past Venus.’

made by Karel van Mander in his *Den grondt der edel vrij schilder-const* published in 1604, and Theodore de Mayerne in 1620. As physician to King James I in London, De Mayerne had come into contact with the court painters.

Van de Passe repeatedly refers to a green that does seem suitable for painting the leaves and stems of plants: Mountain green (*berggroen*). This was the name given to a pigment made from the mineral malachite, a basic copper carbonate, which was however scarcely ever used in oil painting in the seventeenth century. With Rembrandt, Jacob van Ruysdael, Frans Hals, Pieter de Hoogh, Albert Cuyp and many others – including some of the flower painters – one still finds a mixture of blue and yellow.

There were various possibilities for making green from blue and yellow. For the green leaves in a flower still-life Jan Brueghel chose a mixture of stable pigments: the blue azurite, a basic copper carbonate, (crystallographically slightly different from malachite and therefore differing in hue) and lead-tin yellow, a synthetic pigment produced from lead and tin oxides. Balthasar van der Ast, on the other hand, in a flower still-life with shells mixed azurite with an organic yellow dyestuff which, in order to render it suitable as a pigment, was precipitated on alum. Cornelis de Heem used azurite and yellow ochre.

In the painting by Van der Ast the leaves are now bluish, but for a rather different reason than in the case of Van Aelst. Identification of an organic yellow colorant in a painting is difficult and often even impossible. Only the aluminium or alum basis can be demonstrated. The kind of discolouration evident in the Van der Ast painting is comparable to that seen in carpets where the yellow component disappears from the green.

Not only Cripijn van de Passe but also other seventeenth century writers mention the obscure *schietgeel* or *schtgeel*, a dyestuff assumed to derive from an extract of the unripe berries of Buckthorn. De Mayerne writes of it: ‘This colour ... does not tolerate either light or rain; it is

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fugitive, it becomes white, it disappears.’ It is made durable by applying a layer of varnish over it. 16

The yellow colorants used in the seventeenth century were indeed highly sensitive not only to light, but also to lye (alkaline solvents). Chemically these are flavonoids, in which the chromophore – i.e. the part of the molecule responsible for its colour – is easily destroyed by light. Recently conducted tests have shown that they have beautifully transparent, bright colours shortly after their synthesis, but bleach with alarming rapidity and finally disappear. This process is not reversible. The bleaching is strongest in transparent layers, especially where these are applied to a light-coloured underpainting. In such cases, because the light is reflected back by the light underlayer, the destructive effect is double.

For the colour of the leaves in the paintings in the Ashmolean Museum and the Mauritshuis, Van Aelst used the ‘harsh’ Spanish green on ultramarine blue. Van de Passe seems not to avoid the use of Spanish green and advises using it for instance for the asphodel, where ‘the foliage tends almost to blue’17. Spanish green is copper acetate, made by bringing copper plates into contact with vinegar. The raw pigment created by this reaction was then re-crystallised, to be mixed with oil. The chemical product of this process is a copper oleate. Theodore de Mayerne advises using the deep green colour obtained only for the final glazes, for instance of the trees, as some painters do, ‘since it is the enemy of other colours, it kills them all’.18

Leonardo da Vinci also warns against the use of this green in mixtures, suspecting that the paint would quickly turn black.19 As a lake it must be immediately protected by applying a varnish over it or by mixing it with varnish. Varnish or resins are dissolved in organic solvents such as alcohol. Earlier attempts at cleaning could thus very well have caused the partial disappearance of the glaze.

If the glaze consists of Spanish green mixed with oil, under the microscope the pigment can often be found unchanged, usually with a somewhat browned binding medium. During the drying process, the binding medium (oil) is oxidised and partially degraded, among the products of which are the chromophores that give the oil its brown colour. One sometimes finds it recommended in manuscripts to put the painting in the sun, because this will reduce the

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16 De Mayerne, op. cit., note 15. Fol. 11, p. 26. ‘Ceste couleur, non plus que la Lacque n’endure ny l’air ny la pluye, se passe, se blanchit, s’en va.’

17 Van de Passe, Den Blom-Hof, op. cit., note 5, no 36.

18 De Mayerne, op. cit., note 15. Fol. 4, p. 14. ‘Le verd de gris (dont on se sert seulement pour glacer) est tellement ennemy des aultres couleurs qu’il les tue toutes’, fol. 9, p. 22. ‘Quelques-uns glacent leur beaux arbres avec le verd de gris, mais n’oubliez pas d’y mettre le vernis.’

19 Leonardo da Vinci, The literary works of Leonardo da Vinci compiled and edited from the original manuscript by Jean Paul Richter, in two volumes, London 1970, part I, p. 361. ‘Verdigris with aloes, or gall or turmeric, makes a fine green, and so it does with saffron or burnt orpiment; but I doubt whether in a short time they will not turn black.’
darkening. Ostensibly this would seem a good solution, but this is actually not such good advice, for what happens here is that the chromophores are further degraded by the sun.

If the oil has darkened, this has usually happened throughout the entire paint layer. With copper resinate, because it is often only the upper side of the paint layer - which is most exposed to light - that has become brown, sunlight is the most obvious suspected cause. The theoretical explanation (in the field of conservation) for the darkening of copper resinate used to be that the disruptive action of sunlight on the bonding between the copper and the resin caused the copper oxide to be formed. This process would begin on the upper surface of the painting. Given that copper oxide is not transparent, it then acts as a protective layer, resisting the further destructive effects of light. Of course, when looking at a painting it is this surface that one sees, but even if one considers removing the darkened surface layer - against all the rules of the restorer’s profession, in any case – this would be pointless, since the newly exposed surface would once again become brown. However, not only is the process more complicated than this, the darkening may also have a different origins (see the article on the discoloration of green paint in this thesis).

The small painting *A dead hare* by Peeter Snyers also displays the partial abrasion of a copper glaze [4, 5]. Because Snyers had mixed orpiment (arsenic sulphide) with the ultramarine in the underlayer, the discoloration of green to blue is less marked here than with Van Aelst.

Although passages painted in ultramarine sometimes look rather grey as a result of discolouration – specifically known as the ‘ultramarine disease’ – this is not the case with Van Aelst’s underpainting for the leaves. The pigment was normally used only for the glazes, the reason being that it was too expensive to apply it in the whole paint layer, and because of its low refractive index (n = 1.50) it was particularly suitable for use in glazes which were executed in either oil or water binding media on an underpainting of smalt and indigo. The disadvantage of this procedure was that after some time the glaze took on a green appearance as a result of the yellowing of the oil used as binding medium. The blue then discolours to green rather than green to blue as in the painting by Van Aelst. The painters were familiar with this phenomenon and De Mayerne actually recommended using egg white or fish glue, strewn on the dry pigment, instead of mixing it with oil. 20

Smalt is another pigment that played a significant role in the discolouration of blue passages. Smalt was made by crushing blue-coloured glass. The blue in the glass is due to cobalt oxide, which was added to molten glass. Very little cobalt is needed to give the glass a deep blue colour, which has to do with cobalt’s position in the periodic table of the elements.

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If the pigment is ground very fine it is often difficult to discern whether one is looking at discoloured smalt or glass that was colourless in the first place. Finely ground smalt has little colour to begin with and because, like ultramarine, it has a low refractive index, in oil the colour disappears entirely. As with ultramarine, after some time the paint layer becomes greenish or brown as a result of the discolouring of the oil. In addition, with coarser ground smalt, the larger pigment particles can sink into the oil.

Despite the fact that painters in the seventeenth century were aware of these disadvantages, and were specifically warned against them (do not pulverise the pigment too finely, do not use too much binding medium etc.) smalt was very widely used. It was a fairly cheap colouring agent, produced in the Netherlands in the seventeenth century on a large scale for sale both at home and abroad.

Indigo, extracted from plants of the genus *Indigofera*, is another blue colorant that is not entirely colourfast. Although it is a vegetative dyestuff, it is also a pigment – in the sense of the word as used in the art of painting, i.e. it is insoluble in water and does not need first to be precipitated on an insoluble base, as is the case with most other dyestuffs. It can be mixed directly with oil. For its use in the textile dyeing industry it must first be rendered soluble by converting it to the yellowish leuco-indigo, and then oxidizing this to the blue indigo once it has bonded with the fibre. Indigo can bleach if it is exposed to the light, but the ‘discolouration’ of textiles dyed with indigo is for the most part due to the wearing away of the thin layers on the fibres. In paintings one would not expect that kind of wear; when passages where indigo has been used have bleached this must therefore be the result of exposure to light. This discolouration occurs less rapidly than with most other organic colouring agents; the yellow component disappears from the green, but the blue remains – partially at least.
On the other hand we know that this sort of discolouration has to do with the light and with the ambient circumstances of the colouring agent. This means not only the atmospheric conditions but also its more immediate relation to the fibres in textiles or, in the case of paintings, the binding medium and other pigments. Bleaching is a photochemical process, a change in the structure of the molecules caused by the energy of light.

At the beginning of the eighteenth century a new blue pigment was discovered in Berlin. In 1710 this was recommended as an absolutely durable pigment in both oil- and water-based paints, together with an account of the shortcomings of all the hitherto available blues. The process of its manufacture was kept secret until 1724, when permission was finally given for the recipe to be published in the ‘Philosophical Transactions’ of the Royal Society. It was not long before several firms were producing this ‘Prussian blue’ or ‘German blue’ as it was known, in different countries. It has such an intense colour it was said that if a bag of Prussian blue split open a person’s fingers and clothes would also be painted blue. The blue is in fact ferric ferrocyanide, originally produced by chance during an attempt to make a completely different product. It is the first of a long series of modern synthetic pigments. Jacob van Huysum made grateful use of the newly discovered blue, but mixed it with a yellow that has since lost its colour. The result can be seen in a flower still-life in the Fitzwilliam Museum, Cambridge [6]. The discovery of stable green pigments toward the end of the eighteenth century also arrived too late for him. The flower painter Jan van Os mixed Prussian blue with the more stable orpiment, the result of which is that his leaves have remained green to this day.

In all those cases of discolouration and earlier scourings that cannot be undone, the question arises as to whether a painting has to be exhibited in this state. When a minor retouching of the image gives it a greater unity, this may occasionally be the preferred option. But this kind of overpainting is carried out in such a way that it is reversible, i.e. the intervention can subsequently be undone. More usually, however, where the discolouration affects large parts of the painting, the decision is to leave it. Even if we knew exactly what the painter’s original intention was, those who nowadays restore the paintings in public collections would still not try to retrieve the original colour, for the result of that would be a modern painting.