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

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Investigation of the Use of the Binding Medium by Rembrandt

Chemical Analysis and Rheology

As early as the seventeenth century, people were already fascinated by Rembrandt's painting technique. Marshall Smith, an English author writing about this question in 1693, says "Rembrandt had a Bold Free way, colours laid with great Body, and many times in old Men's Heads extraordinary deep Shaddows, very difficult to Copy, the colours being laid on Rough and in full touches, though sometimes neatly finished." Smith must have had Rembrandt's late work particularly in mind. In his essay in the catalogue of the 1991/2 Rembrandt exhibition, Ernst van de Wetering explores this manner of working which was known in the seventeenth century as 'the rough manner'. For anyone alert to it, the technical aspects of this rough manner are to be found even in Rembrandt's earliest work, and according to Van de Wetering, the reason for this was that Rembrandt, from the outset, was concerned with manipulations of the paint surface for expressive purpose. Smooth, shining passages alternated with impasto where the paint can be seen in clots and ridges. The choice depended both on the material to be represented - stone, leather, skin, metal - and on the placings of objects in the light.

Throughout the Rembrandt Research Project, one of the aims has been to gain insight into the materials Rembrandt used and the working methods he applied. Although the original purpose was to gather data that would help to answer questions of authenticity, the broader aspect of the Rembrandt investigation quickly assumed a significance of its own: the data turned out to provide a useful framework within which both to understand phenomena observed in Rembrandt's paintings and to deepen our insight into the technique of painting and studio practice in the seventeenth century in general.

Following the scientific investigation of Rembrandt's panels, the grounds and underpainting and the working method of the first part of Rembrandt's career, it was decided to turn our attention to the binding medium that Rembrandt used. The binding medium is the material in which pigment particles are imbedded and which ensures that the paint dries and attaches to the prepared canvas or panel. It was thought that the question, mentioned above, of how Rembrandt realized the variety of his paint effects might perhaps be answered by this approach.

Previously, such chemical analytical research as had been conducted had led to the conclusion that the pigments and binding medium Rembrandt used to create his illusions did not significantly differ from what other painters of the time had at their disposal. This, however, left open the question of those aspects in which Rembrandt's paintings were different. Since it appeared that the problem would need to be tackled from several different angles, both students of the written sources and those who reconstruct the paint on the basis of the results of scientific analyses were brought together in a single cooperative research project.

With the restoration of the Rembrandts in the Rijksmuseum, a unique situation presented itself where a group of the late paintings could be scientifically investigated by the same people within a limited period and under identical conditions. For the Rembrandt Research Project, there was one aspect of highest priority - the question as to the nature and working properties of Rembrandt's paint, and with particular concern for the binding medium used, the siccatives (driers) and the application of glazing and other effects. Paint samples, usually taken to answer questions raised by the restoration, were sometimes highly informative. For the purposes of restoration, an identical chemical analysis of all the paintings was unnecessary. In relation to the 'binding medium question' too, much greater attention has been paid to particular paintings than to others, for instance to the Jewish Bride and The Syndics. Further comparative data were also obtained from research on samples from other paintings.

The question of how easy the paint was to work, or of the impasto character of the dried paint, also raises the question of whether and, if so, how that might be quantified. This question has to be translated into physical measurements and
impasto, however, it was unnecessary to take a sample of the white underpainting in lead white (basic lead carbonate). In the latter, clots of white paint can be seen under the thin pink and red in the skirt and threads of white paint in the transparent material of the woman’s sleeve. In the Bulletin of the Rijksmuseum, where our research on the painting technique in The Nightwatch was reported, there was speculation over the binding medium used for the white paint in the under layers that was responsible for the impasto character of the surface layer. According to the restorers of The Nightwatch, although lead white forms a particularly tough and flexible film, the white paint in The Nightwatch was softer than one would expect with paint that contained lead white as pigment: for example, the underpainting in the cloak of Van Ruytenburch, which is almost entirely done in white. A sample of the white plume of Van Ruytenburch’s hat revealed 5-10% chalk mixed with the lead white, which expressed in terms of volume is 25% of the dry pigment in the paint. Tests with such a chalk-lead white paint showed that indeed such an addition of chalk makes the paint more viscous (pasteuze) yet without making it difficult to work. In the thick white underpainting of Kemp’s collar and in the helmet of the ensign bearer on the right, however, only lead white was found. The particular, viscous character of the paint was at the time attributed to the addition of chalk and not to the binding medium. Further explanation of Rembrandt’s use of pigments and binding media in achieving his spectacular results would seem to require more research.

Samples were available of:
- the high impasto of the sleeve of the man in the Jewish Bride
- the white paint of the exposed pentiment of a hand in The Staalmeesters
- the shroud in Deyman, the right-hand edge of the picture
- the boot of Van Ruytenburch in The Nightwatch
- the tablecloth in Claudius Civilis (National Museum, Stockholm)
- and for comparison, Ferdinand Bol’s Abraham receiving the three angels (Rijksmuseum), the cloak.

The pigments of the white, thick paint

The paint cross-sections established that under the yellowish and brown brush strokes of the man’s sleeve in the Jewish Bride there was in fact a hidden layer of pure white paint (Plates 2, 3). This paint is strongly outlined in X-radiographs, just like the impasto in The Staalmeesters. In The Staalmeesters the paint investigated turned out to consist of two layers, the uppermost rather more yellowish white, and with a thin, dark brush stroke between them. From the sampling of The Nightwatch it was found that some coloured pigments had been added to the underpainting for Van Ruytenburch’s boot
The paint on the surface of The Nightwatch and in The<br>Staalmeesters is coloured yellow by the addition of a little finely<br>distributed yellow ochre (Plates 4, 5). Two layers were also<br>seen in the shroud in Deyman. X-ray diffraction studies<br>(XRD) and scanning electron microscopy with energy disper-
sive X-ray analysis (SEM-EDX) for the analysis of elements in<br>samples gave the results shown in Table 1, though it will be<br>found that they are not so clear as the table at first sight sug-
gested.18

The percentages of chalk by weight of 5 to 15 %, estimated<br>by XRD, correspond to about 13 to 45 % percent by volume.<br>The conclusion would seem to be that lead white cut with<br>chalk was used for the man’s sleeve in the Jewish Bride. Per-
haps the remark of the seventeenth century painter Wilhelm<br>Beurs has a bearing on this question of the paste white pigment in<br>such a painting as the Jewish Bride where, in De Groote Wae-
reld in ’t keen geschilderd, he says that such an adulterated<br>white pigment is cheap and therefore widely used in less fine<br>and in larger paintings.19 We should not apply this remark of<br>Beurs to the works of Rembrandt uncritically, however, nor

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Plate 1 Detail of the rug on the table in The Staalmeesters.
Plate 2 Detail of the sleeve of the man in the Jewish Bride.
Plate 3 Paint cross-section of sample 40/4b from the sleeve of the man in the Jewish Bride. The sample is incomplete. Pure lead white can be seen underneath a transparent brown paint and varnish. Magnification 200x.
Plate 4 Paint sample 924/48 from the boot of van Ruytenburgh in The Nightwatch. The sample is shown with the whitish underlayer facing upwards.
Plate 5 Cross-section of part of the paint sample in Plate 5, the boot of van Ruytenburgh in The Nightwatch. Layer 1 lead white, a little red and yellow ochre, very little smalt; layer 2 bone black; layer 3 lead white, a little fine yellow ochre. The ground layer is missing. Magnification 200x.
fig 1 Backscattered electron image of sample 40/4b, lead white from the man’s sleeve in the Jewish Bride. Elements with a high atomic number show up light. The binding medium shows up dark.

fig 2 Backscattered electron image of sample 924/48, uppermost layer of lead white in the boot of Van Ruytenburch on The Nightwatch.

fig 3 Backscattered electron image of sample 924/48, underlayer in the lead white of the boot of Van Ruytenburch in The Nightwatch.

fig 4 Backscattered electron image of sample 4/I of the lead white in the exposed pentiment of a hand in The Staalmeesters, upper layer.

fig 5 Backscattered electron image of sample 4/I of the lead white in the exposed pentiment of a hand in The Staalmeesters, underlayer.

fig 6 Backscattered electron image of paint cross-section, sample 5/I of the shroud in Deystan. The darker showing line in the lead white sample is a calcium compound, probably chalk.
TABLE I

Investigation of the binding medium used by Rembrandt

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<tr>
<th>PAINTING</th>
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<th>SEM-EDX</th>
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<tr>
<td>(1642)</td>
<td>85</td>
<td>(Ca) in top layer</td>
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<td>Rembrandt, The Anatomy lesson</td>
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<td></td>
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<tr>
<td>of Dr. Johan (1656)</td>
<td>90</td>
<td>(Ca) in underlayer</td>
</tr>
<tr>
<td>Rembrandt, The Syndics (1661)</td>
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<td>Pb</td>
</tr>
<tr>
<td>Rembrandt, Claude Civilis</td>
<td>85</td>
<td>Pb</td>
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<tr>
<td>(1661)</td>
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<td></td>
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<tr>
<td>Rembrandt, The Jewish Bride</td>
<td>70</td>
<td>Pb</td>
</tr>
<tr>
<td>(c. 1663)</td>
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<td>Ferdinand Bol, Abraham</td>
<td>90</td>
<td>Pb</td>
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<tr>
<td>receiving the three angels</td>
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</table>

* Estimated amounts of lead white, lead carbonate and chalk in weight% relative to the total amount of pigment.

( ) = <1 vol% without looking into the matter further. As can be seen from the table, the result of XRD analysis cannot be confirmed in any of the Rembrandts investigated or in the Bol with SEM-EDX. Under the electron microscope, where elements of high atomic number scatter more electrons and thus show up light in the electron back-scattered image, one can see light, coarse clumps and light, finer granules in the greyish matrix of organic material (binding medium, figure 1). There is a striking similarity between the SEM images of the lead white samples of The Nightwatch from 1642 and The Syndics of 1662. Certainly there is no indication of the twenty year interval between the making of these two paintings (figures 2-5). In the underlayers of both paintings, the lead white appears to be rather more finely ground than in the topmost layer.

Analysis demonstrates that it is not only the areas which show up light that contain lead, but also the grey matrix. A single, darker looking and somewhat coarser particle consists of a calcium compound. The much greater sensitivity of the SEM-EDX technique for lead than for calcium and the similar sensitivity of XRD for lead white and chalk do not seem enough to explain the discrepancy in the analysis results. If it were, in fact, a matter of a cheaper mixture of lead white and chalk, one would expect this to be easily demonstrable with SEM-EDX. A possible explanation presented itself when it was then discovered that a darker row of granules halfway through the white layer in Deyman consisted not of carbonaceous pigment but of a calcium compound, possibly chalk (figure 6). This line, which shows up darker under the scanning electron microscope, is visible with light microscopy as a semi-transparent, yellowy line. It appears that lead white and chalk have been set beside each other in a single stroke of the brush.

The explanation for the higher percentages of chalk shown by XRD must lie in an uneven mixing, a bit of chalk being included by chance in the sample analyzed, whereas the piece selected for SEM-EDX contained only pure lead white. Where a mixture of lead white and chalk - what was in fact known as lead white in the seventeenth century - was used, the mixture of chalk and lead white would be more homogeneous. In the late Rembrandts, apparently pure lead white - known in the seventeenth century as ‘shell white’ - was used in both surface and underlayers. The explanation for the presence of a bit of chalk in the lead white is quite possibly that Rembrandt added a little to his pure lead white on the palette in order to get the consistency he wanted.

X-ray diffraction analysis was also carried out on three samples of lead white recently made according to the ‘Dutch process’, in which thin, rolled-up strips of lead are placed over vinegar in earthenware pots. The three samples were made under differing conditions of temperature, duration and acetic acid concentration. It emerged from the analysis that beside lead white (basic lead carbonate) neutral lead carbonate was also formed in the process. Some 3.5 to 10% neutral lead carbonate was found, the lowest percentage in the sample consisting of soft lumps and powder, the highest in the sample consisting of hard lumps and crystalline powder, corresponding with what was found in the samples from Rembrandt’s paintings. This latter correspondence emerged from microscopic examination of the reference materials: elongated, angular granules up to 20 μm long and crystals of less than 1 μm diameter. The influence of the particle size on the viscosity of the paint will be discussed later in the section on rheology.
The binding medium of the white, pastelle paint - oil

If an electron microscope is used to study a paint sample, one can get an impression of the nature of the binding medium by studying the secondary electron image. In addition, one can tell whether or not a solvent has been used to thin the paint, for the scanning electron microscope allows one to see the topography of the surface studied. In figure 7 of the sample of the white viscous paint of the sleeve of the Jewish Bride an uneven, yet smooth surface can be seen suggesting that the pigment clumps in the sample are surrounded by a binding medium. Small cavities are visible, sparsely scattered and possibly left by an evaporating solvent. More striking are the elongated structures, as though lumps of pigment of similar size have adhered to each other, giving rise to a thread-like structure between the lumps. These threads or rodlets seem to be constructed from segments. They have the same fatty appearance as the pigment clumps embedded in binding medium. Sometimes an entire rodlet is curled up. The white sample from Deyman gives an apparently dried out, crumbly image that has none of the oily, thread-like structure of the Jewish Bride (figure 8). The fact that Deyman has been exposed to high temperatures during the fire of 1723 could account for this.

In order to find out more about the binding medium, another bit of the sample shown on the SE micrograph, taken from the white impasto of the man's sleeve in the Jewish Bride, was analyzed by Jaap Boon using Pyrolysis-mass spectrometry (PYMS) and gaschromatography-mass spectrometry (GCMS) methods. Investigation using PYMS reveals that the binding medium is a polymerised pure linseed oil with a palmitic/stearic ratio of 2.3. There is a relatively high proportion of the di-acid C9 (azelarc) and the ratio C9/C8 is 6.6 (C8/C9/C10 = 5/33/2, GCMS). This would indicate an oil that has not been pre-polymerised by the action of heat. The PYMS analysis further showed that palmitic and stearic acid are present as free acids and scarcely or not at all bound to the polymer oil network. Hydrolysis must have occurred, probably because of the alkalinity due to the lead white (basic lead carbonate). Boon found no wax, though there was a trace of a diterpenoid resin, which could have derived from an old varnish or from the transparent, yellowy-brown resinous paint that lies above the white impasto paint (Plate 3).

The analysis of the impasto of the Jewish Bride turned out to be of special interest. The identification in Boon's analysis of the original binding medium in paint samples taken from coloured passages (i.e. other than the white paint of the impasto) was complicated by elements used during later treatment. In particular, the wax/resin re-linings of the canvases have introduced large quantities of palmitic acid which can create the impression that walnut oil has been used. To prevent distortion of the analysis as a result of contamination by re-lining materials, a comparable sample from a painting on panel must also be analyzed. So far, only the white paint in the sample taken from the man's sleeve in the Jewish Bride has been found to be uncontaminated. The obvious explanation for this is the high pigment volume/concentration of the paint layer containing lead white and its thickness. The re-lining mixture has apparently not permeated through to the top of the impasto.

Linseed oil was also found in the yellowy-white top layer of Van Ruytenburch's boot in The Nightwatch (P/S ratio 2.2) and the white of the tablecloth in Claudius Civilis in the Stockholm National Museum (P/S = 1.7, PYMS). The ratios of C9/C8 di-acids indicate in all cases an oil that has not been pre-treated (not subjected to pre-polymerisation, accelerated oxidation and thickening).

The discovery of linseed oil in Rembrandt's paint layers is not new. Raymond White, in his lecture at the Rembrandt Technical Symposium at the National Gallery in London in 1992, mentioned series of Rembrandt samples in which linseed oil was consistently identified as the binding medium, and occasionally walnut oil. The latter yellows less than linseed oil with age. It would be logical therefore to expect walnut oil to be used for light colours, but this turns out not to be the case. White did find indications that the linseed oil was pre-polymerised, especially where white impasto passages were concerned, as in the Portrait of Frederik Rihel on Horseback and in the Belshazzar's Feast in the National Gallery in London. At temperatures of 270 - 300°C the oil thickens and forms a stand oil - if oxygen is excluded, which is more viscous than the untreated oil. According to White, a non-heated oil was used for yellow impasto paint. Small additions of diterpenoid resin were sometimes found. In their most recent publication, however, White and Kirby propose that the impasto can be obtained either by the use of thickened "heat-bodied" oil or by thickening the paint with pigment or both. They suggest that an oil may well have been boiled, in order to allow mixing with a siccative (a lead compound), at a more moderate temperature of 100 - 150°C.

From the recent test with lead white/linseed oil paint it has been found that made with un-treated (uncooked), cold pressed oil, the paint is a rather 'short', buttery paste whereas with a heat treated oil a paint results with stringy threads. The stringy character was not reduced by the addition of more pig-

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*Plate 3*...
PAINTINGS IN THE LABORATORY: Scientific Examination for Art History and Conservation

All white paint samples investigated for the addition of chalk to the lead white (Rembrandt's The Staalmeesters, Deeman, the Jewish Bride, The Nightwatch, Claudius Civilis, and Ferdinand Bol's Abraham receiving three angels) were also scrutinized for possible addition of proteinaceous materials in the binding medium which, for the most part, consisted of linseed oil. Contrary to the results of earlier analyses by Mills & White and by Boon, which had demonstrated only oil present, high pressure liquid chromatography (HPLC) revealed that protein could be identified in the white pastelze paint of all these paintings (figures 9a – 9k, Table 2).29

For the interpretation of this finding, reference materials such as animal glue, gelatin, egg, purified and non-purified linseed oil, mastic and red dyes of animal origin such as cochineal and kermes were analyzed. In mastic only traces of protein were found, in quantities which, compared with those found in the binding medium, were so small as to be negligible. In all the other reference materials, not only the stable amino acids but also glutamine (GLU), asparagine (ASP), serine (SER) and threonine (THR) could be demonstrated. On the basis of the pattern of amino acids, a clear distinction could be made between protein of animal and plant origin. Glycine (GLY), for example, is clearly evident in material of animal origin, especially in animal glue, and almost absent in unpurified and purified linseed oil. In cold-pressed, unpurified linseed oil, valine (VAL), phenylalanine (PHE), isoleucine (ILE) and leucine (LEU) were clearly demonstrable.

After the oil had been washed with water, HPLC demonstrated that the amounts of amino acid present in the oil was reduced.

Apart from GLY, tyrosine (TYR), VAL, PHE, ISO and LEU were used as indicators. In animal glue, the concentration of GLY is high and TYR low; whereas in egg the concentration of GLY is found to be lower and TYR higher than in animal glue. The concentrations of the later eluting, essential amino acids VAL, PHE, ILE and LEU are also lower in animal glue than in egg (yolk). In particular, LEU is present to a greater degree in egg.

### Table 2

Concentration of the amino acids in mass%. Reference materials gelatin and egg yolk, paint samples 1-9.

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The binding medium of the white, thick paint: proteins

ment. So although the oil is thicker as a result of the pre-polymerization (oxidation) due to the heat treatment, the paint made with such an oil is actually found to be less solid. Tests conducted by Hayo de Boer demonstrate that the higher the temperature used, and the longer the heat treatment, the more stringy the paint becomes.

Pre-polymerizing oil by heat treatment excluding air is a later invention. In the seventeenth century in The Netherlands oil was sometimes thickened while having it bleached by placing it in the sun. Painters saw a disadvantage in the use of sun-bleached oil because such oil suffered from also being thicker. A higher value was attached to a thin, good drying oil especially in animal glue, and almost absent in unpurified and purified linseed oil. In cold-pressed, unpurified linseed oil, mastic and red dyes of animal origin such as cochineal and kermes were analyzed. In mastic only traces of protein were found, in quantities which, compared with those found in the binding medium, were so small as to be negligible. In all the other reference materials, not only the stable amino acids but also glutamine (GLU), asparagine (ASP), serine (SER) and threonine (THR) could be demonstrated. On the basis of the pattern of amino acids, a clear distinction could be made between protein of animal and plant origin. Glycine (GLY), for example, is clearly evident in material of animal origin, especially in animal glue, and almost absent in unpurified and purified linseed oil. In cold-pressed, unpurified linseed oil, valine (VAL), phenylalanine (PHE), isoleucine (ILE) and leucine (LEU) were clearly demonstrable.

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Apart from GLY, tyrosine (TYR), VAL, PHE, ISO and LEU were used as indicators. In animal glue, the concentration of GLY is high and TYR low; whereas in egg the concentration of GLY is found to be lower and TYR higher than in animal glue. The concentrations of the later eluting, essential amino acids VAL, PHE, ILE and LEU are also lower in animal glue than in egg (yolk). In particular, LEU is present to a greater degree in egg.
figs 9a-9k High pressure liquid chromatograms of a) gelatin, b) egg yolk, c) linseed oil, not washed d) white impasto paint in the Jewish Bride e) white paint in F.Bol f) the top layer in the lead white containing paint in The Nightwatch g) bottom layer in the same sample in The Night Watch h) sample of white paint in Claudius Civilis i) white impasto paint in Deyman j) white impasto paint in The Stadmeesters All white paint samples, except Deyman, show high GLU and low GLY, indicating egg. k) sample 4/6 from the smalt-containing grey area of the tablecloth in The Stadmeesters.

High GLY in proportion to GLU and SER indicates the presence of an animal glue in the binding medium of the smalt containing paint.

Since it was not possible to weigh the paint samples and since the paint samples contain a high proportion of pigment, the amounts of proteins present in the reference materials and in the samples can not be compared.
The ratios of the various amino acids found in the lead white paint samples - low GLY, comparatively high TYR, and the concentration of the other amino acids present indicate egg as their source and not an animal glue. Although we did not succeed in making an accurate measure of the weight of the paint samples to determine quantitatively the amount of amino acids in the samples, it can safely be said that a substantial contribution is involved and that the concentration is higher than that found in the unpurified oil. In the painter’s practice, however, this might amount to no more than a minute addition. Perhaps the thread-like, loose structures in the scanning electron micrographs are to be explained by the presence in the oil binding medium of a material that dries rapidly because of water evaporation, for instance egg.

With the help of the sample from the sleeve of the man in the Jewish Bride and the sample from the shroud in Deyman the presence of proteins has been confirmed using staining techniques (the first sample, 40/4b stains strongly positive and the latter, sample 5/1 weakly positive with amidoblock; the other samples have not been investigated by this technique).

It was not possible to infer from the HPLC analyses whether the proteins were in fact derived from egg white, egg yolk, or from the whole egg. Given that egg appears in the paints under investigation together with oil, it would seem obvious that we are dealing with an emulsion paint whose major constituent is oil. This would then be an oil emulsion that could be thinned with a volatile solvent.

In the sources, both egg yolk and egg white - as well as whole egg - are mentioned. From the experimental research of Hayo de Boer it appears that only egg yolk or whole egg are capable of being emulsified with oil. This is the natural conclusion, since egg yolk is the essential component in emulsification.

Rheology

Micrographs were made of details in passages in paintings by Rembrandt, specifically those in which the typical pasteine paint was found. The object here was to make available an atlas of the paint effects to be found in his paintings. A selection of these photographs were submitted to rheologists together with the question of what properties a paint would have to have during its application in order to produce the result shown in the photographs.

Rheologists were approached with this question because rheology is the science which studies the deformation and flow behaviour of materials under mechanical forces. Applying and working up paint, that material is subjected to deformation caused by the mechanical force applied by the hand holding the brush. The reaction of the material can be an irreversible flow, a reversible, elastic deformation, or a combination of the two. The flow properties of a fluid, for example paint, are determined by the resistance of that material to flow i.e. the viscosity, which can be measured, for instance by measuring the resistance to flow when the paint is held between two surfaces. The mechanical properties of an elastic substance can be studied by exerting a force on the substance and measuring its deformation or the stress in that substance. The rheological properties of a material can be graphically represented in a flow curve.

Of course, we are no longer able to conduct rheological measurements on Rembrandt’s paints. However, it was thought that by studying the paint effects on the paintings, more might be learned about that paint at the time of its application.

The rheologists’ response to micrographs of Rembrandt’s paintings was that these clearly showed that very little flow had occurred in the thick paint, which sometimes remains pulled out into threads. After application the paint has remained, as it were, standing. It can be said that the paints used still possessed a considerable yield value. (Materials under tension immediately start to flow once the tension exerted on them exceeds their yield value. Flow also occurs when the yield value is exceeded as a result of the tension due to gravity i.e. they flow under their own weight). Studying both light micrographs and the much more highly magnified electron micrographs lead to the same conclusion. The scanning electron micrograph discussed above under ‘The binding medium’ (figure 7) show that the pigment particles may have the ability to be wetted-out by the binding medium. If we are dealing with an oil paint, the paint must have had ample opportunity to spread, but the electron micrographs show that no such flow has occurred. Trails of paint remain standing and cavities have not been closed by flow.

The size of the pigment particles, as remarked earlier, has enormous influence on the rheological behaviour of a paint.
Plate 6 Detail of the yellow-grey areas in the tablecloth of *The Stoolmeesters*.

Plate 8 Micrograph showing the surface of a sample of a white, deteriorated passage in the tablecloth in *The Stoolmeesters*. Smalt particles show up darker between the brown and the white deteriorating binding medium. Magnification 200x.

Plate 7 Micrograph showing the surface of the deteriorated passage behind the right shoulder of the kneeling soldier, left, in *The Denial*.

Plate 9 Cross-section of paint sample 4/2, from a grey, degraded area in the tablecloth of *The Stoolmeesters*. On the brown ground there occur in sequence a red, a black and again a red paint layer. Above this the remains of a layer which contains mainly smalt. The surface of this paint layer is ruined, smalt particles project from the paint. This is probably the result of previous treatments to which the painting has been subjected. Magnification 500x.

Plate 10 Paint cross-section of a piece of the greyish, degraded surface layer in the tablecloth of *The Stoolmeesters*. The same layer as the uppermost layer in Plate 12 from a different place. The uppermost layer, up to 90 μm, contains smalt in a degraded binding medium which appears white because of the scattering of the light. Magnification 200x.

Plate 11 Cross-section of paint sample 41/6 from the light area with rough cracking behind the right shoulder of the kneeling soldier in *The Denial*. A 70 – 150 μm thick layer of smalt (faded blue and colourless) can be seen in the brown(ed) binding medium. Beneath is the brown quartz ground. Magnification 200x.
Plate 12 Cross-section of a paint sample from the fringe of the tablecloth of *The Staalmeesters*, close to the bottom edge of the painting. On the brown ground containing lead white and umber are separate brown, black and red layers. The uppermost, rather transparent layer could have been mistaken for a coloured varnish. The cross-section shows that it is in fact an original paint layer, in which smalt has been used in a glazing manner. Magnification 200x.

Plate 13 Cross-section of a paint sample 4/10 beneath the right hand of the soldier in *The Denial*. The sample is taken in a passage with wrinkled paint. The cross-section and its analysis show that above a fast-drying, lead white-containing underlayer, there is a non-fast drying layer which contains much ochreous pigment and bone black. A little smalt has been added to this layer, probably to promote drying. Magnification 200x.

The scanning electron micrographs (figures 1 - 6), however, show a great variation in particle size; it is thus the variation which determines the paint’s rheological behaviour. If a distinction is made between the fine powder that occurs in the lead white samples (diameter < 0.1 μm) and the coarse powder (diameter > 0.1 μm, elongated particles up to 20 μm) then it turns out that a dispersion of fine powder in linseed oil gives it a strong elasticity. The coarse particles have no effect on the flow behaviour, they merely heighten the viscosity. Small particles can give to linseed oil a considerable yield value and may lead to the formation of thread-like structures. On the basis of the absence of flow and the presence of very small particles, the paint would seem also to have a considerable yield value. A large variation in particle sizes would favour flow, certainly...
under the high speed (shear rate) with which a painter works his brush.

Subsequently, paints were made up with a composition that could be inferred from the analysis and the historical sources. The tests with HPLC which revealed the presence of the egg component had at that time not yet been completed, so that no account could be taken of proteinaceous substances in the reconstructions and measurements. Measurements of viscosity were made on the reconstructed paint to see whether these produced a flow curve comparable with that hypothesized for Rembrandt's paint. The reconstructed paint ought then to have the same properties as Rembrandt's paint and should not flow at all when applied to canvas. Apart from the rheological measurements carried out, paint was also smeared out to see whether it did indeed remain standing.

Measurements were made on paint prepared with 1) linseed oil with 0.5% lead siccative (lead oxide), 2) linseed oil with 10% by weight lead white, 3) linseed oil with 0.5% lead oxide and 45% by weight finely ground yellow ochre. The linseed oil was (cold) pressed by Hayo de Boer and washed twice with distilled water, drained and filtered. Lead oxide was blended with the oil at 120°C. A concentration of c. 0.5% lead was used on the assumption that a higher concentration would have no further drying effect.

The lead white, prepared according to the seventeenth century Dutch method, was washed with distilled water in order to remove any soluble lead acetate present and pulverised using a muller on a glass plate with a little water until the size of the particles matched those in the paintings. It was then dried at 50°C. For its match with seventeenth century lead white, the presence of coarse and fine particles of the required size was checked under a microscope and the composition of the product was tested using XRD. The size of particles of the yellow ochre did match the bright yellow ochre of the paintings.

In the measurements, it was found that the linseed oil, without addition of any pigment, showed a simple rheological behaviour, as would be expected of a fluid. (If a fluid shows Newtonian behaviour, the rate of deformation is directly proportional to the shear rate, in contrast to non-Newtonian fluids. The higher the shear rate, the higher the force exerted on the material). The Newtonian viscosity — the viscosity of water is 1 milliPascal second (1 mPas) = 1 centipoise — amounted to 47 mPAs after one day and 50 mPAs after a week. A sample of linseed oil to which a large amount of ochre was added showed a strictly non-Newtonian behaviour. There was a high yield value and the material was highly deformable but reversibly so, with the material later recovering its original form. Blending ochre with oil produced a thixotropic paint, a paint with a structure which tears during application but which recovers again (either rapidly or slowly) when allowed to stand. All concentrated dispersions with fine particles show thixotropic behaviour. The paints measured in this experiment recovered very rapidly. It is true that they did not run and the brush stroke remained visible, but it was a very short paint to work with, quite unlike the long threads that could apparently be drawn out with Rembrandt's paint.

The measurements subsequently carried out on the lead white paint gave results indicating paint systems whose rheological behaviours varied from viscous fluids to rather strong elastic materials which also showed thixotropic behaviour. When these paints were smeared out, after a certain time they did not spread any more because of drying effects. When extra pigment was added, the paint became rather crumbly and no longer properly workable. After thinning, as probably also happened on the palette, it handled better once again.

Transparent paint layers

Smalt and lead compounds

In the late Rembrandts, passages occur which, before restoration, appeared to be deteriorating badly, such as the tablecloth in The Staalmeesters (Plate 6), the foliage in the flowerpot on the right in the Jewish Bride and ill-defined passages behind the right shoulder of the soldier on the left in The Denial (Plate 7). The paint layer in these passages turns out to contain smalt that was almost completely colourless as the main constituent. Smalt, i.e., finely ground cobalt-coloured glass, has a low refractive index and together with the binding medium produces a layer of paint with rather poor covering properties (Plates 8–11, figure 10). The disintegration of the paint layer must be the result of an interaction between the smalt and the binding medium. The now indeterminate colour of the paint layer must originally have been transparent and have had something of a blue tint. In fact, cobalt could still be demonstrated. The fact that, in Rembrandt's paintings, layers rich in binding medium often contain large quantities of glass such as smalt, has been previously shown.

There are various reasons to assume that, in employing smalt, Rembrandt's main concern was not primarily the (pale) blue colour. In the yellow of the leaves in the right-hand background of A young Monk (Titus), the small amount of smalt added to the strong yellow can still be explained as a means of getting a green from yellow and blue, the usual practice of Rembrandt and other painters of the seventeenth century. In differently coloured passages, on the other hand, the colour effect of the smalt must have been minimal, as for example in the brown glazing layer of the fringe of the tablecloth in The Staalmeesters (Plate 12, figure 11), in a comparable brown layer that is found on the deep red of the tablecloth (sample 4/7, above the signature) and in the transparent brown paint on the thick, impasto layer beneath the right hand of the soldier in The Denial (Plate 13). The particles also appeared in brown and red paint layers that seem to be intended as underlayers for further layers of paint, as can be ascertained in the bald patch behind the soldier's neck in The Denial (sample 41/7) and in the tablecloth of The Staalmeesters, where the remains could be found on the smalt layer of an apparently largely disappeared, transparent red layer of paint. The smalt-containing paint layer is often thick (up to 150 μm). Such a layer must have been intended as an underlayer to give volume to...
non-covering glazing layers. Sometimes, it seems, such a paint was also used as a finally applied glaze.

Indications that smalt was used in underlayers can also be found in the sources. It turns out that as a result of washing the smalt, prior to drying and blending with binding medium, different qualities were obtained, the lesser of which were found adequate for underpainting in certain passages: \( \text{The first, second and also the third washings of the Smalt are suitable for laying the dead colouring for landscapes,}^{43} \text{ Sometimes it was recommended to mix fresh (i.e. finer) ground smalt into the smalt to get faster drying.}^{49} \text{ The catalytic action of cobalt that occurs in smalt at the interface between the pigment particles and the oil binding medium is greater the larger the surface area, hence with smaller particles. With coarser small particles the interface area is apparently insufficient for rapid drying.} \)

Apart from their greyish, deteriorating appearance, these passages also often show a pattern of coarse cracking, which in principle would suggest a too rapid drying of the smalt layer. In the tablecloth of \( \text{The Staalmeesters,} \text{ the red paint of an underlying layer has reached the surface through the cracks of the already dried smalt layer. Cobalt compounds are still considered the best siccatives. They promote surface drying and if used as the sole dryer, it can happen that the paint layer remains soft beneath a tough skin of hardened paint.} \)

To allow the paint film to dry properly throughout, combinations of lead and cobalt are used nowadays. SEM-EDX analysis of Rembrandt’s paints showed that lead was absent from the smalt or glass particles, which is of course only to be expected when one considers that lead glass only came into use in about 1670. In a paint layer containing no lead pigment, therefore, one can look for any lead dryer that might be present in the oil binding medium between the particles\(^{40}; \text{ and indeed, using SEM-EDX, lead was demonstrated in the binding medium in \( \text{The Staalmeesters (sample 4/2, figure 12), The Denial (sample 41/6) and the Jewish Bride (sample 40/7, figure 13).} \text{ The use of oil with lead siccative was established using the same technique in a comparable sample from \( \text{Esther before Haman from Bucharest.} \text{ The concentration of lead in the oil in these samples must be greater than 0.5\%.}^{41} \text{ There is also evidence for Rembrandt’s use of oil siccativised with lead in other coloured passages than the smalt layers. Lead was found in the deepest black layer of paint (bone black) in the cloak of \( \text{A young Monk (Titus) (sample 2/3 (4)) and in the red glaze of the woman’s cloak in the Jewish Bride (Plates 14, 15).} \text{ Lead was also found in the quartz ground of \( \text{The Nightwatch,} \text{ and in the ground of the Self-portrait as the apostle Paul,} \text{ which for the most part consists of chalk. Since lead white never seems to be involved, the presence of lead indicates a drying oil prepared with lead oxide.} \)

 provisionally, it looks as though uncooked linseed oil was used for rapid-drying pigments like lead white, while for non-drying pigments a lead dryer was cooked with the oil. In this latter group, the cooking temperature was kept moderately low.

In \( \text{Esther before Haman,} \text{ not only was lead found in the binding medium between the particles, but also copper. Copper compounds are sometimes recommended in the sources for drying. The presence of copper in the binding medium, however, could also be explained as deriving from the copper container in which the oil was normally placed in the sun as part of the preparation procedure.}^{42} \)

Under long-wave UV irradiation, the layers rich in binding medium, and containing smalt, show a yellow fluorescence round the small particles which is visible in the paint cross-section under the light microscope, while the rest of the binding medium remains dark. This indicates that the main constituent of the binding medium is oil (dark under UV). The presence of fatty acids was established by microscopic Fourier Transform Infrared Spectrometry (FTIR). In addition, the presence of sugars was demonstrated, probably derived from a gum (-OH and C-O absorption bands occurring together, sample 4/6, figure 14). The gum constituent of the binding medium is probably the fluorescent material round the small particles. Using HPLC, an animal glue was also demonstrated in the smalt layers of \( \text{The Staalmeesters.}^{43} \text{ Since tests show that it is not really possible to make smalt into a workable paint with oil alone, the gum constituent must have been incorporated with the oil to ensure that an emulsion-like paint could be produced using smalt.}^{44} \)
Red glaze

Before beginning to remove the varnish from the *Jewish Bride*, the binding medium of the red of the bride’s cloak was analyzed. While studying the brush stroke in the *Portrait of Jan Six*, Max Doerner had noticed that the paint had hardly flowed at all in application, and drew the conclusion that it must have congealed immediately after being applied. According to him, this was a strong indication that Rembrandt’s medium must have been of a resinous nature. He suggested that Rembrandt had used thick oils blended with Venetian turpentine. This pronouncement, ever since the publication of Doerner’s book in 1921 has had huge consequences for the approach adopted by cleaners of Rembrandt’s paintings. Any paint layer containing resin would be in danger of being removed together with the varnish if the painting were cleaned using an organic solvent. According to Doerner’s ideas, the use of resinous paints would apply particularly to superimposed glazing layers such as the bride’s red cloak.

In the paint cross-section it can be seen that the red passage was first sketched in a thin red paint (Plates 14, 15), above which darker underlayers, possibly modelled, were introduced before the cloak was painted in vermilion (mercuric sulphide). Above the orange-red vermilion was set a dark red glaze in which carmine, an extract from the cochineal insect, was used as the colouring element (identified by thin-layer chromato-
Micrograph, using a confocal laser microscope (DSM-Research), of a cross-section of a sample of the red glaze in the Jewish Bride. This photograph demonstrates that the cavities occur deep within the sample, well below the surface of the paint layer on the painting.

Under the light microscope, and even more clearly under the electron microscope, unusual and striking cavities can be seen in the red paint layers and most especially in the red glaze. Under a confocal laser microscope it was possible to demonstrate that the cavities are not only to be found in the surface of the preparation, but throughout the entire transparent red paint layers. There are round and oval spaces varying from a few microns to c. 20 μm, sometimes with encapsulated substances, in a tight film (figures 15 - 17). It was shown by EDX-analysis that the inorganic constituents both within and outside the cavities were the same. The cavities do not seem to be the result of the rigors of a former treatment but are rather suggestive of the original consistency of the paint. It seems we may be dealing with a two-phase system, for example water emulsified in oil. The paint seems to have congealed before enclosed air bubbles, or water droplets or solvent, could escape.

De la Rie and Boon identified a drying oil, probably linseed oil, in the red glaze and in its underlying layer of vermilion. The wax and di- and tri-terpenoid resins also present should probably be attributed to a re-lining and not taken to be an original constituent of the binding medium of the red glaze. Using SEM-EDX, lead was demonstrated in the red glaze, undoubtedly a lead dryer of the type already described. An interesting discovery is that of the presence of sugars. According to Boon (note 8) the complex polysaccharide, identified as cherry gum and present in the red glaze, is likely to be an original Rembrandt contribution to the drying oil of the glaze.

The addition of gum could well be the explanation for the cavities seen in the paint layer. The light microscopic image of the cavities certainly looks like water droplets emulsified in oil. A water solution of the polysaccharide obtained as a gum from cherry trees easily emulsifies oils and resins, sticks very well to oil paint layers and dries to a clear translucent layer.

Cherry gum is mentioned in written sources in connection with the manufacture of red ink, by Carel Baten, for instance, in 1600 and by Simon Eikelenberg in the last quarter of the seventeenth century. Other gums, such as gum arabic and tragacanth are mentioned in other sources, sometimes for quite different uses than in painting. Sometimes the addition of honey instead of gum is mentioned, as in a recipe by Van Veen for making "vetten olijf: make linseed oil and put in a clean, earthenware vessel. Put a some goat schuwum (gold scum) together with some umber and a little honey under the oil, boil together and allow to stand quietly, then strain off the oil (goat schuwum is a dryer, probably lead monoxide). If the gums, and possibly also the honey, were dissolved in water, this would produce together with the oil an emulsion-like paint which would be highly suitable for making a glaze. A glazing layer must be applied thickly in order to give sufficient force of colour. Through the addition of water (with the dissolved gum), the paint would have more volume than just an
organic pigment in oil alone. And indeed, the red glaze on the
Jewish Bride is thick.

Although resins were identified in the red glaze, not as original
constituents but as material subsequently introduced, this
had no significant consequences for the cleaning. The resin
was present in a very low concentration and not as a main ingre-
dient as Doerner had suggested. The presence of gum in the
paint layer alters its solubility properties: the polar nature of
its constituent sugar molecules notably increases the paint's so-
lubility in that most polar solvent, water.

Other aspects of the painting technique

Grounds

The Still life with peacocks has a coloured double ground with
a red-brown ochre (bound with glue?) and above it a brown-
grey layer of oil paint with lead white, umber, charcoal black
and a little red ochre. This type of double ground was used by
Rembrandt in the thirties, giving an upper ground layer that
was somewhat lighter in colour. The Portrait of Johannes
Wittenbogaert, also painted in the thirties, acquired by the
Rijksmuseum during the restoration of the seven late paint-
ings, also turned out to have been executed upon such
grounds. The ground of The Staalmeesters likewise consists
of two layers, but here the composition and colour are differ-
ent from the grounds of the early works on canvas. On The
Staalmeesters, the undermost layer consists of chalk with
umber and the upper layer of lead white, a little chalk, umber
and a trace of red ochre. The greyish ground of A young Monk
(Titus) correspondingly has the same two layers, the under-
most of chalk and umber, the upper of chalk, lead white and
umber. The ground of the Self-portrait as the apostle Paul was
found to have but a single layer, consisting of chalk to which
red and a little yellow ochre has been added.

Grounds of the so-called «quartz type» occur in the Jewish
Bride and the Anatomy lesson of Dr. Deeyman. The ground ma-
terial, applied in one layer, consists for the most part of quartz
(Plates 14, 16). In the Deeyman, parts of the red-brown ground
are now exposed at the surface of the painting as the result of
the fire in 1723 and the treatment it suffered during the conse-
quent restoration. Under the stereomicroscope, the ground is
seen to contain scattered, relatively coarse sand grains. In the
brown ground of The Denial the quartz seems to be a natural
constituent of brown and red earth, the pigments which, in
various quantities together with chalk and a carbon black,
Rembrandt used as his ground. From the early forties, Rem-
brandt frequently painted on grounds that consisted for the
main part of quartz. The Nightwatch, for example, also has
such a ground.50

The evidence of this research indicates that a paste made of
quartz and a quantity of brown ochre with sometimes also a
little lead white, and bound with drying oil, seems so far to
have been used exclusively by Rembrandt and perhaps his stu-
dio. The reason for using quartz (sand) is probably that it was
needed to make a paint with which the unevenness in the
weave of usually relatively large canvases could be subdued.

The same rationale, Van de Wetering has suggested, underlies
the use of double grounds; this allowed first a cheap red earth
to be used before the relatively more expensive, lead white-
containing second ground was applied to get the right colour
to paint on.51

In order to learn more about these quartz grounds, special-
ists in sedimentary geology were consulted.52 The quartz par-
particles in the Rembrandt grounds vary from c. 5 to 60 µm corresponding with silt grade sediment, which contains particles from 4 – 63 µm diameter. Since only silica occurs in these particles, we are not dealing with clay. A study of scanning electron micrographs of a sample of the ground of the Jewish Bride (figures 18 – 21) shows that, at least in the case of the larger quartz grains, the surface of the grains is hardly curved. The material, therefore, before being used in making ground paint, must originally have consisted of rather larger grains, possibly up to 2 mm diameter. The surface of the particles shows V-shaped pitting and grooves, indicating subjection to mechanical violence. If one looks at the form of the particles under SEM it can be seen that there are also particles with very sharp points. The edges of some particles show conchoidal fracture planes that could only have arisen through cracking. On the SE micrographs of these preparations, apart from the sharp fragments of larger grains, there are also small granules to be seen of only a few microns diameter which have no sharp edges, but appear rounded by natural forces. It is implausible to suppose that the mixed grades of the quartz or sand particles in the bulk of the ground is the result of deliberate mixing by the grinder or painter of different grades of sand. Rather, it can be inferred that the starting material for the grounds was poorly (naturally) sorted sand.

Pits and grooves in the surface of sand grains indicate their collision with each other as the result of wind or water transport. If this occurs in the 'poorly sorted' sand where particles also show sharp fractures, apparently the result of mechanical force, then it must be supposed that we are dealing with glacially deposited sand which has undergone the shearing forces of the ice which transported it from its place of origin, not wind or water.

The difficulty is that nowadays, and in all probability in the seventeenth century too, only natural material from Antarctica has this appearance. The material transported from Scandinavia to the Netherlands at the end of the ice age has over the course of time been further abraded by wind and water transport with consequent rounding of particles.

The sand with its irregular grain size which served as the starting point for the ground of some of Rembrandt's paintings must therefore have been cracked in some other way to render it fine enough to be worked in a ground material. It was apparently made fine enough by rubbing or grinding on a grindstone or in a mill, where the force thus exerted on the grains would compare with that of a thick layer of ice. In fact, by being pulverized in this way, the sand that was to be used as filler in the ground was subjected to the same treatment as the minerals that were used as colour pigments in the paint layers.

Sand of this quality must have been easily accessible in Amsterdam. It was used as the raw material in the building and pottery industries. (In Amsterdam's glass-making industry the raw material was glass).

Chemical analysis of the quartz particles showed that the sand was extremely pure. Finely rubbed, it must have had a white colour. Since quartz has a low refractive index, mixed with oil it would have formed a colourless and transparent mass. Probably this was the reason brown ochre was added in order to get a brown painting ground.
The aim of this article was to reflect the state of affairs in the research on the binding medium of the paint used by Rembrandt for the paintings in his late period. The idea was not to make a definitive pronouncement on the subject; the extent of the results of analysis obtainable is too limited for that. It is in fact self-evident that taking samples, as regards both their number and size, has to be restricted, in spite of the importance of the analysis, whether for the purpose of this research or for the restoration of the paintings. In the course of the research, furthermore, it became evident that reaching conclusions about Rembrandt's binding medium was complicated by the paintings themselves from which the samples derived, since these were paintings on canvas which had a whole history of restoration behind them. The results of analysis that were obtained related both to (aged) original material and also material later forced into the paint layer. This too helps to make interpretation of the results more difficult.

Despite the limitations, we propose the following, cautious conclusions. The binding medium used by Rembrandt – as far as we know in his late period – consists chiefly of a drying oil with small additions of other organic ingredients. The results of analysis indicate that the binding medium was modified for the differently coloured passages and for the different textures.

The existence of recipes for the rendering of different passages in a painting was earlier suggested by Van de Wetering, on the basis of the palettes depicted in studio scenes. Van de Wetering demonstrated that only those pigments and mixtures of pigments that were necessary for painting a particular passage were carried on the palette. The chemical analysis of the paint layers that has now been carried out allows the conclusion that each passage to be painted was not only prepared separately as far as the pigments were concerned, but that each such pigment mixture also had its own binding medium: the oil binding medium was modified for each pigment. More samples of the different colours need to be investigated using the same techniques for pigment, binding medium (the main constituent and organic additives) and dryer. The results obtained in this research are set out in TABLE 3.

The reason for the existence of individual recipes for the mixing of pigments for different colours may have been an economic one. Where the binding medium used for a particular pigment is concerned, there would have been a technical necessity, since some pigments cannot be worked into a suitable paste for the painter to use in oil alone. In such cases a little gum or honey was added in the mixing the oil binding medium with the pigment. It is also possible that further ingredients, such as glue or egg, may have been added on the palette during the actual painting.

According to Pacheco, dryers were also ranged on the palette. He says that materials which promote drying, for example lead pigments, glass, smalt or umber, were first warmed up with linseed or walnut oil, cooled, and then in small globs placed on the palette. Many colours not only had their own binding medium but also their own dryer. Even during the washing of the pigments, the actual washing agent used – pure rain water or acetic acid – would depend on the particular pigment.

In an investigation of the paint of Van Eyck, Brinkman, after a rather limited number of analyses, arrived at a similar working hypothesis of an adaptation of the binding medium. According to Brinkman, Van Eyck used a fatty emulsion for his modelling layers, based on a lead siccativised oil emulsified with egg. For the more superficial glaze, a 'pure' lead oil was used, except with blue. For blue glazes, the binding medium was egg white-tempera. Small details were executed with lean (egg white) binding medium, and for highlights a gelatinous binding medium was sometimes used.

The present research in Rembrandt's paint has revealed the use of more ingredients than were found with Van Eyck – cherry gum is an example. One explanation for the discovery of different organic constituents in Rembrandt's paint is that more and more refined analytic techniques have been employed in the Rembrandt research. Alternatively, more ingredients were actually added in the seventeenth century; but whether or not this was actually the case cannot at the moment be said.

Brinkman suggests that the use of paint was simplified after Van Eyck. In the seventeenth century, for example, egg was no longer added to lead oil because, as a result of the evolution of oil painting, from painting in tempera, via tempera/oil in the time of Van Eyck to pure oil painting in Rembrandt's time, when the point of adding egg to the oil binding medium was no longer understood. One reason, however, must certainly have been clear: without these additives lead oil quickly browned and cracked. Whether the addition of egg – indeed, we know in Rembrandt's case that this only happened with lead white paint with untreated oil – changed the consistency is a matter that is now being investigated further using rheological tests. We hope, as a result, to strengthen our interpretation of the results.

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Above all, I am deeply indebted to DSM in Heerlen, who has given support to scientific research for the Rembrandt Research Project since 1990.

Notes


6. Karin Steenbeck, in a research project under Prof. E. van de Wetering, has investigated the written sources on the use, purification and drying of oil. In the context of a subsidiary of his subject, chemistry, G.G.A. Meiers has carried out a preliminary investigation, under Prof. E. van de Wetering, that resulted in: *En opzet om de door Rembrandt bereide verven te reconstrueren*, Amsterdam, 1989 (unpublished). Studies of the literature and sources were also conducted by Hayo Menso de Boer (under intern supervisors Prof. E. van de Wetering and Dr. E.J. Sluiter), who also began to reconstruct the paints used. (Unpublished report, 1989). See also the pioneering work on drying oils by Renée Keller, *Leinöl als Malmittel*, *Maletechnik*, 2 (1973), pp. 74-105.

7. The following paintings were restored: *A Young Monk* (*Titus*), 1660, *Still Life with two dead Peacocks and a Girl*, c. 1639, *Self-Portrait as the Apostle Paul*, 1661, *The Syndics* (*The Statesmeesters*), 1662, *The Denial*, 1666, *The Jewish Bride*, c. 1665, *The anatomy lesson of Dr. Johan Deyman*, 1656, *Wittenbogaert*, 1633. Restoration reports will appear in *Restauratie Jaarboek*, vol. 1, *De Acht Rembrandts* (Amsterdam: Rijksmuseum, 1997). The analysis of varnish layers and other surface layers—for the purpose of restoration—was carried out by the Central Laboratory for Research of Objects of Art and Science in Amsterdam, since April 1997 the Netherlands Institute for Cultural Heritage. Thin-layer chromatography was by W. Roelofs, Fourier Transform Infra-red Spectrophotometry was by R. Karremans, microscopy and staining techniques by M. de Keijzer. The results of these and other analyses have been assimilated and discussed in the restoration reports in *De Acht Rembrandts*.

8. The chemical concern DSM in Heerlen, The Netherlands, has given financial support to scientific research for the Rembrandt Research Project since September 1990 and has furthermore made the research facilities of DSM Research in Geleen available. Medium analyses were done also by Prof. Dr. J.J. Boon, FOM Institute for Atomic and Molecular Physics and Dr B. de la Rie, National Gallery of Art, Washington. The results of analysis will be published in J.J. Boon, J.B.M. Peerveen and D. Raimond, *Direct Temperature Resolved Mass Spectrometry of the Mobile and Chemically bound Organic Constituents in Rembrandt's 'Jewish Bride'*, and E. Rene de la Rie, Karin Groen, Manja Zeldenrust and Michael Palmer, *An Investigation of some of the Paint Binding Media of Rembrandt's 'Jewish Bride'*, Applications of Pyrolysis-Gas Chromatography and other Micro Analytical Techniques, both in *Restauratie Jaarboek*, vol. 1, *De Acht Rembrandts* (Amsterdam, Rijksmuseum, 1997).


11. Raw oil pressed from linseed contains, in addition to glycerides and their hydrolysis products, a number of other constituents that have a considerable influence on the properties of the oil. These include proteins, carbohydrates, phosphatides and small amounts of other substances. To purify the oil it was washed in water. To accelerate the purification, absorbent materials were added. In written sources, the following are mentioned for this purpose: bread crumbs, sawdust, burnt bone, pumice powder, lime, salt, sand, alum, urine.

12. Van de Wetering, op. cit. note 2, see illustrations on pages 14, 15, 34 and 35.


14. Paint samples, depending on the question and the relevant technique of analysis, consist of a small scraping of the surface of the paint or of a section taken through all the layers. The surface of a sample is about 0.25 mm². Cross-sections of paint and other sample material are being kept in the Central Research Laboratory for Objects of Art and Science in Amsterdam.

15. Van de Wetering, op. cit. note 2, site of sample on p. 35, figs 52 and 53.

16. The sample from *The Nightwatch* has been kept in the Central Research Laboratory since the restoration of the painting in 1976. The sample from *Claudius Civilis* was sent to us during treatment and investigation of the painting in Stockholm in 1993. Ferdinand Bol's *Abraham receiving the three angels* was restored by the Limburg Restoration Studio Foundation in Rolduc.

17. The build-up of the layers corresponds closely with that in the sample from the yellowish boots of Van Ruytenburch in *The Nightwatch* (sample 924/48), from which it may be concluded that the
underlying hand in *The Staalmeesters* was already at the stage of being worked up when Rembrandt decided to paint it out. Ernst van de Watering, *De jonge Rembrandt aan het werk*, *Oud Holland*, 91, Nr 1/2, 1977, pp 46-60. E van de Watering, *Painting materials and working methods* in: B Bruyn et al note 3, vol 1, pp 11-33.

18 X-ray diffraction was carried out by P. Halbeek, Central Research Laboratory for Objects of Art and Science. The proportions of components present were subsequently estimated and expressed in percentage by weight. The apparatus consists of a Philips generator, type PW 1011/02 with a copper anode diffraction tube. The monocromatic CuK radiation is the sole wavelength transmitted by a Ni filter. A small Debye-Scherrer camera was used (R=5.729). SEM-EDX recordings and analyses were carried out by Mrs A Bronnenberg, DSM Research, using a Philips SEM 515, EDAX PV 9800. For the scanning electron micrographs, samples were coated with Au/Pd for the secondary electron image and with carbon for the back-scattered image. The secondary electron image shows the topography of the surface of the sample, the back-scattered image gives information on the atomic weights of the elements present.

19 W. Beurs, *De Grote Watered in 't kleen geschilderde..., Amsterdam, 1692, p 9,* "...To Goede ongemalen Loodwit bereid men op dezelfde wize als het Schulpwit, dog 't is gemakkelijker om vrijen, en alzoo het mede onkostelijker is, daarom 't is zeer eikelijk in gebruik, en wel in min keurige en in grootere schilderijen, zijnde anders in witheld en beslagacht, met name hoe bene ren het schulpwit zekerhij te stellen." (One prepares well mixed lead white in the same way as shell white; though it is easier to grind. It is also cheaper, and therefore more widely used, particularly the less fine or larger paintings, being otherwise in whiteness and in durability of the paint certainly inferior to shell white).


23 Boon op.cit, note 8: Samples are investigated using temperature resolved pyrolysis mass spectrometric (PYMS) analysis, a direct mass spectrometric technique which elucidates the nature of the chemical constituents as well as the way in which the compounds are chemically bound. With this technique the weakly bonded molecules adsorbed onto mineral surfaces are released and volatilised at a low temperature, whereas molecules chemically bound in polymers require bond dissociation at a higher temperature before they are released from the sample matrix.

*Main peaks in the spectrum of the white in samples 40/3a are m/z 206 and 208 from lead and m/z 44 from CO2 released from carbamides and carboxyl groups. Other main peaks are m/z 256 and 284 from palmitic and stearic acid (ratio 2.3). Palmitic and stearic acid appear to be entirely free or very weakly bonded because they show up early in the temperature profile. There is a substantial polymeric phase, however, which is obviously responsible for the relative strength of the paint.*


24 The term "stand oil" is these days used for oil inspissated (thickened) by heating without oxygen present. In the seventeenth century however, the term was used for oil that inspissated through precipitation and the uptake of oxygen, by allowing it to stand in the sun.


Stand oil has certain advantages compared with raw linseed oil that has not been pre-polymerized. The presence in it of large molecules makes for better spreading, which gives rise to a high gloss film.


29 HPLC was carried out by Bea Munsters, DSM Research. HPLC conditions:

- Hydrolysis 24 hours at 110° C;
- Hewlett-Packard type 1090 liquid delivery system;
- Column: Machery & Nagel, 25° 0.4 cm ID nucleosil 120-5-C18;
- flow rate 1 ml per min;
- temperature 40° C;
- injection volume 20ml;
- detection by Hitachi spectro-fluorometer: type F-1550;
- excitation wavelength 335nm, emission wavelength >370nm;
- Gradient elution:
  - eluent A: 50m sodium acetate buffer pH 6.0, using acetic acid; eluent B: 66.6% MeOH, 33.3% eluent A;
  - eluent C: 95% MeOH, 10% eluent A.
  - 0 min 99%A 1%B 0%C
  - 10 min 99%A 0%B 100%c
  - 70 min 99%A 0%B 100%c
  - 85 min 0%A 100%B 0%C
  - 85.5 min 99%A 1%B 0%C
- Pre-column derivatization by o-phthalaldehyde (OPA)/β-mercapto- propionic acid (MPZ). Manual derivatization is necessary because of the small amounts of sample available.
- 8.3 ml of a 0.56 mol MPZ/MPZ in 1 ml MeOH/H2O = 1:1:2.0 ml of a sample solution (made up in 0.4 M boric acid at pH 9.4, by titrating NaOH), reaction time 5 minutes.
- Before injection, the reaction mixture was neutralized by addition of 33 ml 0.25 M phosphoric acid.

Although the important amino acids proline and hydroxyproline, present in animal glue, cannot be demonstrated with this technique as used by DSM Research, the method was employed nonetheless. It was a technique already in operation at DSM Research and required little modification. Only the manner of hydrolysis needed to be adapted for the analysis of minute amounts of sample. The modification was carried out following S. Halpene (see note 30).

We are not aware of any research by others involving the use of HPLC to identify proteins in samples of Rembrandt's paint. The amounts present are probably too small to be identified in the GC-MS analysis for oil and with FT-IR, the methods usually employed for medium analysis.

Boon has evidence for a protein marker with PYMS in sample 40/4a of the *Jewish Bride*. Boon op. cit, note 8: *Mass spectrometric profiling* of the data set in search for protein additives, for example m/z 117 indicative of tryptophane, and other protein indicators at m/z 67.
I am most grateful to Susan Halpine for her critical comments on the results. Halpine recommended also running a reference sample of caseine in connection with high GLU. She also pointed out inconsistencies in the proportions of amino acids which can arise through interference by pigments in the analysis. Copper pigments, in particular, can strongly influence the amino acid pattern. Copper was not, however, present in the samples analysed.


I am grateful to Dr H.C. Booij, Dr M. van Gurp and J. Palmen, of DSM-Research for rheological measurements, for advice and interpretation of the results.

Measurements were carried out by J. Palmen with a Böhm VOR rheometer and with a RMS 800 mech spectrometer.


SEM-EDX analyses could be carried out on areas with a cross-section of <2 µm, where it was possible to analyse both the middle of the small particles and the coloured edge. Just as much cobalt was used in the additions of sodium and potassium oxides that were earlier necessary, for example, in Venice in connection with high GLU. SEM-EDX analyses of grounds showed that lead was also used for quartz grounds, for example on Flora in the Auctioneer in the Metropolitan Museum in New York (sample codes ZL6 and YL5 respectively). Traces of lead were found in the chalk ground in the Self-Portrait in the MET, perhaps for the same reason (sample YL7).

Tests show that it is not really possible to make a good, workable paint out of small and oil alone. The paint does not have the right viscosity, the grains appear to sink. (Oral communication, Margriet van Eikema Hommes.) Although the sources give no indication for the addition of egg (white) to oil, there was a tradition of preparing blue pigments with an aqueous binding medium. See, for example, no. 86 of De Mayerne in Van de Graaf, op. cit. note 27.


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