National Gallery Technical Bulletin

Volume 20, 1999

Painting in Antwerp and London: Rubens and Van Dyck

National Gallery Publications
London

Distributed by
Yale University Press

Series Editor: Ashok Roy

First published in Great Britain in 1999
by National Gallery Publications Limited
St Vincent House, 30 Orange Street
London WC2H 7HH

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

ISBN 1 85709 251 1
ISSN 0140 7430
525278

Edited by Diana Davies and Jan Green
Page make-up by John Gibbs
Printed in Great Britain by BAS Printers Limited,
Over Wallop, Hampshire

Front cover
Anthony van Dyck, Detail of Lady Thimbelby from *Lady Elizabeth Thimbelby and Dorothy, Viscountess Andover* (see Plate 34, p. 74).

Page one
Peter Paul Rubens, Detail from *'Peace and War'* (see Plate 1, p. 90).

Van Dyck's Paint Medium

RAYMOND WHITE

ANALYSIS of Van Dyck's paintings in the National Gallery Collection by gas chromatography (GC) alone, gas chromatography –mass spectrometry (GC–MS) and Fourier transform infra-red spectrometry (FTIR)–microscopy has shown that the artist used linseed oil to a very large extent; the results of analysis are tabulated in detail below. The sample of paintings examined is small compared with the painter's output as a whole, but it seems that for the paintings produced during the artist's period in England from 1632 until his death, linseed oil was his preferred medium. Walnut oil does occur, in yellow paint on the subject's shot pouch in *William Feilding, 1st Earl of Denbigh* (NG 5633) for example, but infrequently. Van Dyck used walnut oil to a greater extent in the paintings produced in Italy, and also in those like *Charity* (NG 6494), which were produced in Antwerp and Brussels after his return from Italy in 1627. Sometimes the oils were heat bodied; for example, heat-bodied walnut oil was used for George Gage's black robe in *Portrait of George Gage with Two Attendants* (NG 49), painted while the artist was in Rome. Heat-bodying in this instance would help to offset the tendency of organic black pigments to inhibit the drying process in oil paints, often causing paint film defects.

Van Dyck's discussion with de Mayerne on the use of an aqueous medium, such as gum or glue, for blues (and mixed greens), followed by a varnish, has been discussed above (see p. 15); in so far as it was possible to examine passages of blue or green paint, analysis of the paintings in the National Gallery Collection has revealed no evidence whatsoever of this practice.

Examination of the Table will show that Van Dyck added a trace of pine resin to the paint used for red glazed passages on drapery. In addition there is evidence for the use of heated pine products, typically softwood pitch, in brownish glaze paints from the *Portrait of George Gage*, *The Balbi Children* (NG 6502) and the *Equestrian Portrait of Charles I* (NG 1172). Heating resins or resin-containing materials was a typical way to produce translucent, brown-black tars and pitches, which could be used in a similar way to asphaltum or bitumen.

Plate 44 Anthony van Dyck, *William Feilding, 1st Earl of Denbigh* (NG 5633), *c.*1633–4. Canvas, 247.5 × 148.5 cm. Birch bark tar was used for the golden-brown glaze on the servant's tunic.

Another variety of translucent brown, also produced by heating – not, in this case, resinous material, but wood or bark – was bistre, a form of tarry soot. It was used in *William Feilding, 1st Earl of Denbigh* (Plate 44).

Results of medium analysis

Picture	Sample	Medium
The Emperor Theodosius is forbidden by Saint Ambrose to enter Milan Cathedral NG 50 canvas *c.*1619–20	1. Thin warm glaze-like shadow-paint plus opaque black paint in shadow of step 2. Golden-coloured trimming on shoulder of Saint Ambrose's robe 3. Grey paint of architecture, upper right-hand edge 4. Red glaze paint of the Emperor Theodosius' robe	linseed oil, heat-bodied with traces of lower hopanes and pine resin[1] partially heat-bodied linseed oil linseed oil partially heat-bodied linseed oil + a little pine resin
Portrait of Cornelis van der Geest NG 52 oak *c.*1620	1. White impasto of ruff, to right of sitter's head 2. Fragment of greenish(?) brown/black from edge (added surround) 3. Black from shoulder, quite opaque	heat-bodied linseed oil partially heat-bodied linseed oil + a little pine resin[2] partially heat-bodied linseed oil
Portrait of a Woman and Child NG 3011 canvas *c.*1620–1	1. Sample of lower ground 2. Rich, wine-red glaze paint of drape, upper left-hand side 3. Shadow paint (opaque) of black satin dress, lower right-hand edge 4. Dark blue paint of distant landscape, to left of sitters	partially heat-bodied linseed oil[3] partially heat-bodied linseed oil + a little pine resin[4] heat-bodied linseed oil[5] linseed oil, partially heat-bodied[6]
Portrait of George Gage with Two Attendants NG 49 canvas probably 1622–3	1. Sleeve of black robe (sitter's left arm) 2. Right-hand attendant's brownish cloak (shoulder) 3. Cream-coloured impasto of distant sky, left-hand edge (above horizon) 4. Blue sleeve, attendant at extreme right	walnut oil, heat-bodied heat-bodied linseed oil with a trace of asphaltum or bitumen and a little heated pine resin[7] heat-bodied walnut oil partially heat-bodied linseed oil[8]
The Balbi Children NG 6502 canvas *c.*1625–7	1. Ground sample 2. Red glaze paint of right-hand child's dress (mid-tone) 3. Sky, mid-left-hand side 4. Flesh paint of right-hand child's left hand 5. Foliage of tree in background, seemingly dark brown	linseed oil[9] drying oil (linseed, or walnut – or a mixture of both) + traces of pine resin[10] linseed oil, no resin[11] partially heat-bodied walnut oil heat-bodied linseed oil with a little pine resin pitch[12]
Charity NG 6494 oak *c.*1627–8	1. Light brown ground + some dark blue underpaint and ultramarine glaze on top, from blue drape, left-hand side 2. Darker, more opaque paint from blue drape, left-hand side 3. Greenish-brown glaze, lower left-hand corner 4. Dark brown shadow of drapery 5. Dark brown glaze-like paint of background, left-hand side 6. Wine-red glaze paint of Charity's robe, right-hand side	partially heat-bodied walnut oil[13] partially heat-bodied walnut oil[14] heat-bodied linseed oil + lignitic earth(?)[15] analysis unsatisfactory through instrument failure[16] heat-bodied linseed oil with traces of pine resin and lignitic earth(?)[17] partially heat-bodied linseed oil + a little pine resin[18]
William Feilding, 1st Earl of Denbigh NG 5633 canvas *c.*1633–4	1. Green leaf, lower right-hand edge 2. Blue-green leaf, adjacent to sample 1 3. Yellow paint and warm glaze paint of back of servant's tunic 4. Brownish leaves, lower left-hand edge 5. Cool yellow highlight of shot pouch hanging at the Earl's right side	partially heat-bodied linseed oil partially heat-bodied linseed oil, rather lean, somewhat degraded medium[19] heat-bodied linseed (or linseed + walnut) oil with birch bark bistre[20] partially heat-bodied linseed oil heat-bodied walnut oil[21]

Picture	Sample	Medium
Carlo and Ubaldo see Rinaldo conquered by Love for Armida NG 877.2 oak 1634–5	1. White highlight of drape associated with putto, lower right-hand corner	heat-bodied walnut oil
	2. Brown shadow, lower right-hand corner	partially heat-bodied linseed oil
	3. Ground, from extreme edge, right-hand side	chalk ground and a protein-based binder by FTIR– microscopy
The Abbé Scaglia adoring the Virgin and Child NG 4889 canvas 1634–5	1. Dark green paint of drape behind the Virgin's left shoulder	linseed oil[22]
	2. Black(?), opaque outline paint from the Virgin's left shoulder, from a rather thick impasto stroke	partially heat-bodied linseed oil
	3. Beige ground, from unpainted corner	partially heat-bodied linseed oil
	4. Mustard impasto highlight of yellow cloud, to upper left of centre	heat-bodied linseed oil
	5. Bright blue (ultramarine) sky, upper left	partially heat-bodied walnut oil
	6. Dark blue of the Virgin's robe, with glaze paint	heat-bodied linseed oil[23]
	7. Purple-coloured sky, left-hand side	partially heat-bodied drying oil[24]
	8. Warm brownish-black glaze paint of shadow from fold in pink sleeve of the Virgin's dress	heat-bodied linseed oil + some pine resin + lignitic(?) earth pigment[25]
	9. Pink/red glaze paint of non-shadow area, adjacent to fold in pink sleeve of the Virgin's dress	partially heat-bodied linseed oil, with a trace of pine resin
Lady Elizabeth Thimbelby and Dorothy, Viscountess Andover[26] NG 6437 canvas *c.*1637	1. Warm glaze paint in darker shades of Lady Dorothy's yellow gown	linseed oil, heat-bodied + a little pine resin
	2. Opaque, yellow principal layer of paint from Lady Dorothy's gown	partially heat-bodied linseed oil[27]
	3. Fragment of brown-red ground, with greyish priming	partially heat-bodied linseed oil[28]
	4. Dark semi-opaque brown of background, lower left	heat-bodied linseed oil with traces of asphaltum/bitumen[29]
	5. Red silk drape around winged putto	partially heat-bodied linseed oil + a little pine resin
	6. White of sleeve of Lady Dorothy's dress	heat-bodied linseed oil
Equestrian Portrait of Charles I NG 1172 canvas *c.*1637–8	1. Warm white impasto stroke of distant white cloud just above horizon on left-hand edge	heat-bodied linseed oil
	2. Warm brown glaze-stroke, over lower part of crimson silk garment of the equerry	heat-bodied linseed oil + a little pine resin
	3. Green leaves of foliage, lower right-hand side	linseed oil[30]
	4. Warm glaze paint toning over rock, lower right-hand side	heat-bodied linseed oil + some partially heated pine resin or pitch[31]
	5. Yellow highlight paint stroke of stirrup	heat-bodied linseed oil
	6. Dark greyish blue of distant landscape, left-hand side	heat-bodied linseed oil[32]
	7. Pale crimson paint of equerry's sleeve	partially heat-bodied linseed oil, with a trace of pine resin
	8. Rich blue sky, lower left-hand edge	heat-bodied linseed oil
	9. Fragment of warm greyish ground	partially heat-bodied linseed oil
Lord John Stuart and his Brother, Lord Bernard Stuart[33] NG 6518 canvas *c.*1638	1. Brown-black paint of background, left-hand edge, above elbow	linseed oil + birch pitch[34]
	2. Yellow brocade wrap over upper arm of Lord John Stuart	walnut oil + birch pitch
	3. Red-brown lining of drape, same figure	linseed oil
	4. White highlight of Lord Bernard's grey silk sleeve	walnut oil
	5. Black shadow in fold of silk jacket, same figure	linseed oil + birch pitch
	6. Blue paint of cloak, same figure	linseed oil

Notes and References

1. Lower right-hand side. Components containing base peak of *m/z* 191 and seemingly lower norhopanes, possibly resulting from heated forms of asphaltic and bituminous pigments. See R. White, 'Brown and Black Organic Glazes, Pigments and Paints', *National Gallery Technical Bulletin*, 10, 1986, pp. 58–71.
2. This sample is from the later (1637) addition to the panel.
3. Infra-red microscopy indicated that drying oil was present as binding agent. The mineral content appeared to be calcite mixed with some silicates. This would appear to be some form of calcium carbonate-based silicaceous earth.
4. The lower part of this partially separated sample seemed more opaque (containing vermilion, principally), but with a little red lake. Here the medium proved to be partially heat-bodied linseed oil, with barely a trace of pine resin. This is in contrast to the lake-rich glaze paint above, with a more heat-bodied linseed oil and a more pronounced content of pine resin.
5. A fragment of upper ground or priming seemed to be present below this sample. However, its composition by FTIR–microscopy seemed to be different from that in sample 1 (the lower ground) in that it was a mixture of lead white and brown, with some black pigment, bound with drying oil.
6. There seems to be smalt in this and an isolated 'clump' of indigo particles, using FTIR–microscopy.
7. This sample consisted of a warm glaze paint (containing evidence of possibly heated asphaltic material, from lower hopane homologues), with a lower, brown, opaque paint and surprisingly an orange-red paint below this. An attempt was made to crudely separate the brown, more opaque paint and the orange-red material (vermilion + red lake pigments) below. GC–MS indicated the presence of a partially heat-bodied linseed oil, possibly with a trace of pine resin. However, the chromatogram also admitted evidence of a trace of larixol and another (possibly related) ketol. On balance one, or both, of the lower layers (perhaps relating to a previous composition on the added canvas section) seemed to possess paint media containing partially heat-bodied linseed oil with larch resin, or a mixture of larch and pine resins.
8. Seemed to have a greyish ground; the palmitate/stearate ester ratio value of the medium was on the linseed/walnut oil boundary (GC–MS analysis). However, linseed oil – partially heat-bodied – appeared to be the medium of the bulk of the principal layers of paint.
9. A cream-coloured ground and apparently a single layer. FTIR–microscopy indicated calcium carbonate and silica/silicate composition, presumably some form of carbonate-containing earth. Only drying oil was detected within the binding medium; there was no evidence of proteinaceous amide bands.
10. Partially heat-bodied drying oil, with a palmitate/stearate ester ratio of 2.0. This could be either linseed or walnut oil, possibly a mixture of both in view of the other results from this picture. Traces of pine resin were detected in the paint by GC–MS.
11. FTIR–microscopy revealed that some brownish-grey material present was discoloured smalt in a drying oil medium.
12. FTIR–microscopy showed a rather dark organic matrix, some brownish particles and some verdigris particles. Heat-bodied linseed oil was identified by GC–MS. From the GC–MS total ion chromatogram, evidence of a trace of simonellite (and retene, too) suggested a minor addition of partially tarred softwood resin/pitch. This would seem an unsuitable component, if the leaves were intended to be green originally. The resin was distributed throughout the medium rather than added as a 'copper resinate' pigment.
13. FTIR–microscopy confirmed that indigo pigment was present in the dark blue layer, with a medium of drying oil. The pale blue ultramarine glaze appeared to contain a drying oil binder as well. No layers of glue or gum-like materials were detected as potential isolating material around the ultramarine pigment.
14. FTIR–microscopy confirmed indigo pigment to be present in the sample. Although there was no sign of a distinct boundary, nevertheless subtraction of the contribution from the 'core' of the pigment, and partial removal of the (drying oil) medium-rich areas, left a spectral residue with a certain similarity to that encountered in polysaccharidic materials. This may represent 'gummy' impurities brought down on the surface of the crude indigo particles – equally, it may represent a treatment of that pigment with a plant-gum extract. Notably, this was not found to be the case for the ultramarine particles present in sample 1.
15. This sample appeared to contain green and brown pigments, possibly Cassel earth. Following analysis by GC–MS there was an indication of the use of heat-bodied linseed oil: no resin, softwood pitch or any of the usual hopane homologues were detected in this sample. Interestingly, a subsequent ion scan for *m/z* of 109 revealed a vestigial peak of almost identical retention time to that component found in sample 5 (see note 17 below).
16. This sample of paint appeared to be a dark yellow-brown glaze, with a few opaque particles and traces of red lake beneath. FTIR–microscopy indicated the medium to be essentially drying oil.
17. 7-oxodehydroabietic acid indicated the presence of a conifer resin (most probably from *Pinus* sp.). Traces of three components, with (B^+) *m/z* = 109 and (M^+) *m/z* = 262 with peaks at *m/z* = 191, 219, (B^+) *m/z* = 259 (M^+) *m/z* = 274 (minimal), and (B^+) *m/z* = 95, (M^+) *m/z* = 276 with a strong *m/z* = 247, were present. These components would appear to correspond with fichtelite and possibly the dihydro- and tetrahydrorimuenes, which might result from the inclusion of some form of lignitic earth.

18. A tiny fragment of double ground was present at the bottom of this and had broken away. A warm cream-coloured ground appeared to contain oil, but a cooler, greyish lower ground gave some indication of protein amide bands, probably glue, upon examination by FTIR–microscopy.
19. This paint had a somewhat blanched appearance. There appeared to be some particles of yellow lake here, too.
20. It was not possible to separate the warm glaze-like paint from the yellow, more opaque paint. GC–MS indicated that the medium was composed of (essentially) heat-bodied linseed oil, but that the palmitate/stearate (P/S) ratio was at the upper limit for that material, in contrast to the other samples from this work containing linseed oil. In view of the medium analysis for sample 5, a mixture of linseed and walnut oils (the latter possibly originating from the opaque yellow paint) appears likely. Traces of betulinic acid were detected and another triterpenoid acid, possibly betulonic acid from its fragmentation pattern. This might suggest the presence of a heavily oxidised birch bark tar component or a birch bark bistre, but there are complications in the form of rather polar components which seemed to produce rather poor chromatographic and spectral peaks following GC–MS analysis. They were resolved – to some extent – only after acidification of the TMTFTH-treated remnants and examination by gradient elution, reversed phase HPLC (high performance liquid chromatography). These components appeared to be phenolic and correspond to syringyl and ferulyl fragments, most likely resulting from the inclusion of degraded lignin in the material. From this we may infer that actual birch wood (from which betulin is absent, but lignins, based on ferulic and syringic component polymers, are present) was mixed with the corresponding bark, from which the betulin and its subsequent oxidation products, but not the lignin, originate.
21. Some slightly opalescent inclusions, within the body of the paint medium, were examined by FTIR–microscopy and were found to be occluded regions of fatty acid carboxylates. Given the asymmetric carbonyl stretching frequency, measured as *c.*1510–12 cm^{-1}, with the corresponding symmetric carbonyl stretch at *c.*1400–7 cm^{-1}, it would seem that this material represents occlusions of metal soaps. Lead soaps appear to have a lower asymmetric carbonyl stretching frequency than the corresponding alkali metal soaps, which appear in the mid-1500s cm^{-1} region.
22. FTIR indicated the presence of indigo dyestuff as well as some particles of yellow lake. This was mixed with lead-tin yellow pigment, to produce green.
23. Both samples 5 and 6 contained ultramarine, with the addition of some indigo in the latter. Despite careful examination by FTIR–microscopy, no evidence of a proteinaceous or a gum-based medium or pigment-isolating layer was found to support the use of such materials in conjunction with ultramarine-based paints as mentioned by de Mayerne (see p. 15 of this *Bulletin*).
24. The palmitate/stearate ester ratio measured by GC–MS was at the walnut/linseed oil boundary – possibly a mixture of the two is present, with linseed dominant.
25. A trace of a component with a mass spectrum resembling fichtelite was detected by GC–MS.
26. These represent further results, obtained by GC–MS and FTIR–microscopy on fragments remaining from the 1977 (GC analysis only) sampling campaign. These media results were reported in J. Mills and R. White, 'Organic Analysis in the Arts: Some Further Paint Medium Analyses', *National Gallery Technical Bulletin*, 2, 1978, p. 74. Linseed oil was identified in yellow highlights of Lady Dorothy's dress and in a white sleeve as well as in a green drape in the background.
27. Two slightly opalescent inclusions within the body of the paint medium were examined by FTIR–microscopy and were found to be occluded regions of fatty acid carboxylates. See note 21, above.
28. FTIR–microscopy pointed to the use of a drying oil medium in both ground and priming layers.
29. This sample area corresponded with sample 3 (dark brown of background, lower left edge) in the 1977 campaign. At the time, using GC only, it was felt that some asphaltic material might be present in view of poorly resolved high retention time peaks emerging after the main chromatographic run. Lower hopane homologues were identified by GC–MS in the current study, which suggest the presence of a heat-treated asphaltum or bitumen.
30. This paint appeared slightly blanched and discoloured.
31. Inferred from the presence of dehydroabietic and 7-oxodehydroabietic acids, simonellite and traces of retene in this sample, following GC–MS examination.
32. FTIR–microscopy indicated the presence of some smalt in this sample.
33. A detailed study of this picture was reported in R. White and J. Pilc, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 16, 1995, pp. 90–1 and note 24, p. 95.
34. Some signs of paint shrinkage in this area.