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Garry Thomson, Scientific Adviser

Martin Wyld, Chief Restorer

Ashok Roy: Editor

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The Mediums used by George Stubbs: Some Further Studies

John Mills and Raymond White

In Volume 4 of this *Bulletin* [1] the results of studies on the medium of George Stubbs's *Lady and Gentleman in a Carriage* (No.3529), were reported. Samples from some other late period paintings by this artist have since been examined, resulting in a clearer picture of his techniques, and these studies are reported here. They also led to a re-examination of samples from the above painting with some modification of our interpretation of the findings. Some of the new results, given in an interim report, have appeared elsewhere [2].

The results and their interpretation in [1] were based primarily on gas-chromatography supplemented with examination of the samples on the microscope hot-stage. Our new results have been obtained utilizing the greater sensitivity of detection and surer identification of peaks afforded by combined gas-chromatography-mass-spectrometry (GLC-MS) [3]. There is no need to describe these methods again here but a few words must be said concerning the chemical natures of the four classes of materials which seem to have been used in the mediums, and the overlap in the chemical

make-up of three of these four which can make the interpretation of analytical findings difficult and uncertain.

The materials involved and their distinction

The raw materials which are thought to have been found in Stubbs's paint medium are drying oil, non-drying oil or fat (or the free fatty acids derived from these), beeswax, and pine resin. The detection of this last depends on finding certain diterpenoid resin acids. These are not components of the oils, fats and waxes and their presence affords an unambiguous detection of the resin. With dried drying oil, non-drying oil and beeswax the main components (after saponification) are the same for each, namely palmitic and stearic acids. Fortunately drying oil also shows a high proportion of the dicarboxylic acid, azelaic acid, and consequently a fair proportion of this allows the detection of drying oil in the presence of the other two. The distinction between non-drying oil and beeswax, or the detection of mix-

Figure 1 Chromatogram yielded by beeswax after saponification and methylation. E (signifying ester) is followed by the carbon number of the acid. H, for hydrocarbon, is followed by its carbon number.

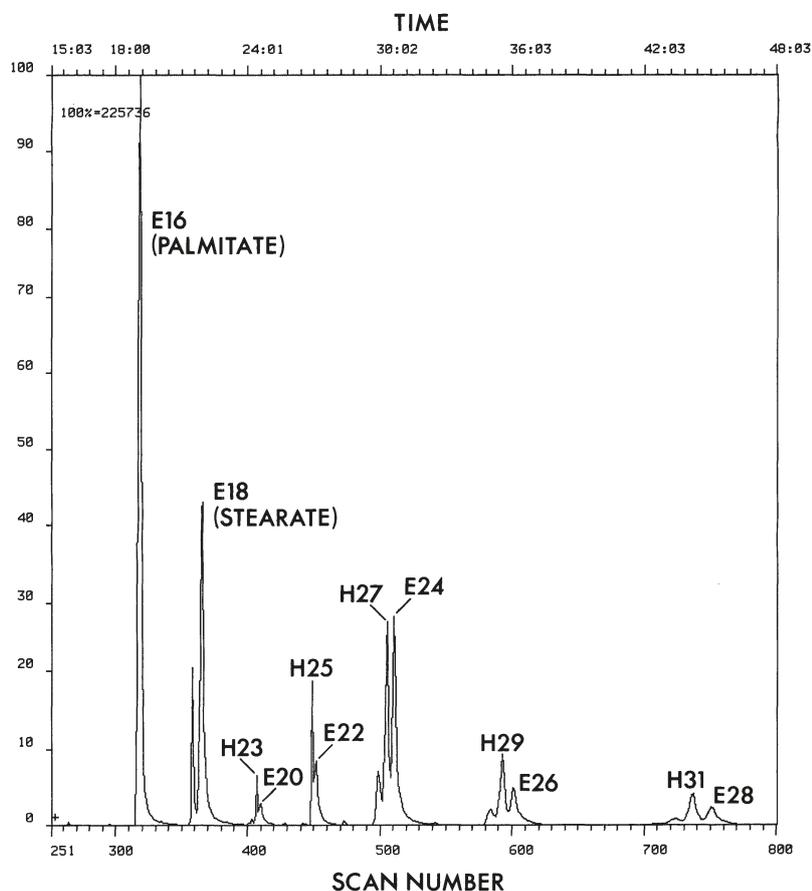


Table 1 Components identified in the medium of ten paintings by George Stubbs.

Title	Owner	Date	Support	Ground?	Medium Components			
					Drying oil	Non-drying oil/fat	Beeswax	Pine resin
The Charger Ridden by Henry Fellowes. . .	Private Coll.	1772	panel	no			+	+
Shark	Private Coll.	1775	panel	no		+		++
Horse in the Shade of a Wood	Tate Gallery	1780	panel	no			+	+
The Reapers	National Trust	1783	panel	yes	+		+	+
Lady and Gentleman in a Carriage	No.3529	1787	panel	yes	+		+	+
Warren Hastings on Horseback	Private Coll.	1791	panel	no	+		+	?
Fino and Tiny	H. M. the Queen	179(?)1	canvas	yes	+		+	trace
The Phaeton	H. M. the Queen	1793	canvas	yes	+	+ or	+	+
Soldiers of the 10th Light Dragoons	H. M. the Queen	1793	canvas	yes	+	+ or	+	+
Hambletonian	National Trust	1800	canvas	yes	+		+	+

tures of the two, is more tricky however. Beeswax may readily be identified in its raw state by gas-chromatography if sufficient sample is available [4] and it was sought for in this way in our first examination of samples from No.3529 but without positive result. The amount present in a small paint sample may well be insufficient. Saponification of beeswax liberates a large amount of palmitic acid (roughly 20% of its weight [5]) and a lesser proportion of stearic acid and unless other more specific components are also observed the former acids could equally originate from the alternative sources mentioned. Fortunately saponified beeswax does also show a pattern of higher fatty acids accompanied by characteristic hydrocarbons, as may be seen from Fig.1. After the stearate peak the even carbon-number esters increase in concentration, reaching a peak with the C₂₄ acid ester. The hydrocarbons likewise show a distribution pattern peaking at C₂₇. The presence of these patterns has been found to be a sensitive indicator of the presence of beeswax in paint samples and the pattern may be shown up, even in chromatograms where the peaks themselves are not clearly discernible, by means of scans for mass 74 (the base peak for fatty acid methyl esters) and 57 (a strong peak in the mass spectra of the hydrocarbons though less exclusive than mass 74 for esters). This will be exemplified for actual samples below. It should be said, however, that the higher esters are not absolute proof of the presence of beeswax since they are also found in small amounts both in drying and non-drying oils. The pattern is different though: the amounts diminish progressively with increasing molecular weight and there is very little C₂₄ acid ester but of course this does add to the uncertainty when mixtures are in question.

Analytical results

Table 1 summarizes our results for ten Stubbs paintings between 1772 and 1800. All were examined by gas-chromatography, and all except *Warren Hastings on Horseback* and *The Phaeton* were also examined by GLC-MS. In most cases at least three samples were examined from each painting. The results were not necessarily identical in each group, and in particular proportions of ingredients could vary, but they did not conflict with one another and could reasonably be generalized as indicated. It is quite possible that where beeswax is indicated, non-drying oil or fat could be present as well for this would affect only the fatty acid proportions. There is, in fact, a likelihood of this in the case of the newly examined samples from the *Lady and Gentleman in a Carriage*. These had rather high proportions of stearate (Fig.2) which could be the result of additions of animal fat or, indeed, the stearine wax which we postulated in our first publication [1]. There is no doubt now though that beeswax is present (Fig.3).

It will be noticed that the paintings' techniques fall rather clearly into two categories. The earliest three employ no drying oil and are painted in a medium of wax-resin, or non-drying oil/fat-resin, on panels without a prepared ground, in the usual sense of that term. *Shark* is somewhat different to the other two and we have naturally looked carefully at the results to see whether they could be interpreted as beeswax rather than oil/fat but the pattern of hydrocarbons and higher fatty acids could not be found. This medium contained an exceptionally high proportion of pine resin, rather well-preserved.

The paintings from *The Reapers* of 1783 onward show another pattern. They contain the same components as the above three but now with an addition of drying oil. The particular oil cannot be specified as the palmitate/stearate ratios are changed by the presence of

Figure 2 Chromatogram of paint of blue sky from Stubbs's *Lady and Gentleman in a Carriage* after saponification and methylation. The peaks following stearate are identified in Fig. 3.

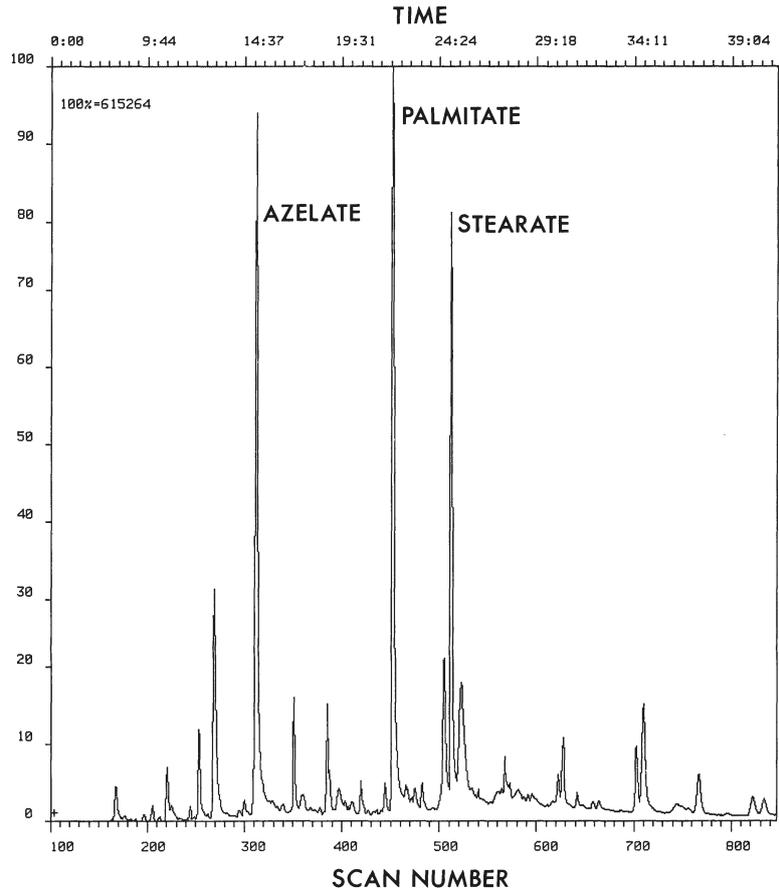
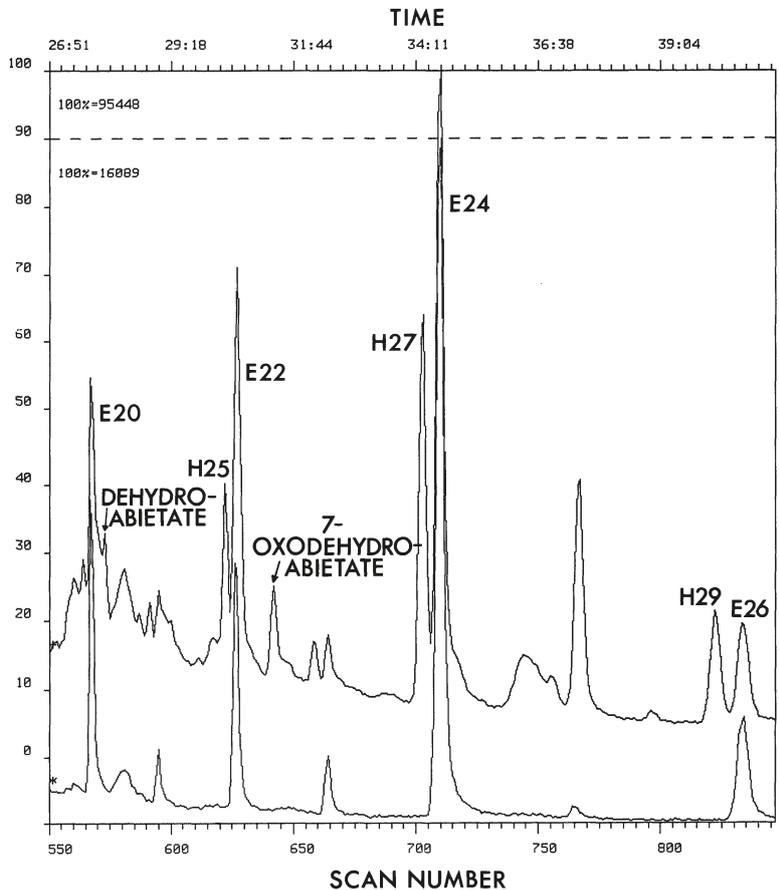


Figure 3 Post-stearate section of the chromatogram of Fig. 2. A scan for mass 74 (lower curve) picks out fatty acid esters revealing a pattern, maximizing at the C₂₄ acid ester, typical for beeswax. The odd carbon-number hydrocarbons are also observed as are small quantities of dehydroabietate and 7-oxodehydroabietate from pine resin.



the other components. In the case of *The Soldiers of the 10th Light Dragoons* the samples were rather small and the results were ambiguous as concerns the distinction between non-drying oil/fat and beeswax. The appropriate higher esters were present but not in the expected proportions for beeswax, and the pattern of hydrocarbons could not be distinguished. *The Phaeton* was not examined by GLC–MS but the same components as in *The Soldiers* are ascribed on the basis of it showing the same gas–chromatographic peaks.

Where the medium of the ground in these latter paintings has been examined it has seemed to be the same as that in the paint layers. In the earlier group on panels without grounds there is some indication that the panel was first treated with a coating of the wax–resin mixture. A scraping from the bared wood surface of *The Charger Ridden by Henry Fellowes at the Battle of Minden 1757*, in an area of paint loss, certainly showed wax–resin but this might also simply have transferred itself from the (now lost) paint. Another factor which must not be entirely lost sight of in considering these analytical results is that of possible contamination by the materials used in conservation treatments of these sometimes quite damaged paintings. In general though the overall consistency of the findings would seem to discount this. How the wax–resin medium may have been used to paint with will appear in the next section.

Possible origins of Stubbs’s techniques

The primary purpose of this article is to present analytical results. A full investigation of Stubbs’s influences lies in the domain of the art-historian but we would like to point out here the interest which existed in Europe, in the second half of the eighteenth century, in the encaustic technique attributed to the Ancient Greeks and in its reconstruction in some form applicable to panel and canvas paintings.

In 1755 the Comte de Caylus presented a paper to the Académie des Belles-Lettres of Geneva on his interpretation of Pliny’s references to painting with wax and his experiments in practising the method. This was written up and published with a collaborator [6]. He examined several different possible approaches which cannot easily be summarized but essentially they involved an initial preparation of the support (panel or canvas) by waxing with the aid of heat; painting on this waxed surface with the pigments in various possible media (see below); heating the finished painting, in front of the fire or with small portable braziers, to melt the wax and unite the paint and preparation. The frontispiece (Fig.4) epitomizes the procedure. The medium for application of the pigment could be an aqueous one and consists either of water on its own or containing a little dissolved gum. This was proposed as the probable classical approach since it involved only materials available to the Ancients. Alternative media which Caylus tried, and which were successively displaced as imperfect, were: beeswax dissolved, or partially dissolved in oil of turpentine (not very soluble so too low a proportion of wax to pigment resulted); beeswax melted with non-drying oil or fat such as olive oil or lard (too sticky); beeswax melted with resins, either pine resin as it came

from the tree known as turpentine or gallipot (mixture rather sticky) or as the residue from this after the distillation of oil of turpentine known as colophony (mixture rather brittle); a final, perfected, mixture involving beeswax mixed with ‘varnishes’, incorporating resin and non-drying oils as above, of several compositions, diluted with oil of turpentine as required. The remainder of the book is given over to discussion of the pigments which may be used with this technique and an account of the history of its development and practice by the author and others.

A book in English on Caylus’s techniques [7] appeared in 1760. The author dismisses the use of elaborate mixtures as being an unnecessary complication and reduces the procedure to the following:

First. The cloth or wood designed for the picture is waxed over, by only rubbing it simply with a piece of beeswax.

Secondly. The colours are mixed up with common water; but as these colours will not adhere to the wax, the whole picture is to be first rubbed over with Spanish chalk, or whitening, and then the colours are used.

Thirdly. When the picture is dry, it is put near the fire, whereby the wax melts and absorbs all the colours.

In 1770 appeared yet another commentary on Caylus [8], praising him for his ingenuity in quest of the true method but saying that he had nonetheless failed to arrive at the best solution. This was simply to combine



Figure 4 Frontispiece to Caylus’s book of 1755 [6]. Minerva (or Pallas Athene, identified by the owl on her helmet), Goddess of the Arts and Sciences, calls the artist’s attention to the putti who are assisting with the final, heat fusion stage of the encaustic procedure. In the background are bees and beehives, the source of the wax.

oil paint with an equal quantity of wax! Practical details are lacking, however, in this lyrical but prolix work.

A further book on the subject, by the expatriate Spaniard, Vincenzo Requeño, appeared in Italian in 1784 [9]. It is of tedious length, the second volume being largely devoted to the controversy regarding the composition of 'Punic wax' and other peripheral matters, but the author does give recipes and methods (some similar to, others even more involved than those of Caylus) and he claims to have practised the technique himself with great success. The book has two attractive engravings showing painting in progress and the final heat treatment.

This brief survey probably does not exhaust the literature on the topic of encaustic painting current in the 1770s and 1780s but it suffices to indicate the very close parallel between the methods suggested in it and the components of Stubbs's mediums which we have detected by analysis. Stubbs's changed painting techniques came about shortly after his first essays in enamelling and we suggested in our first article that he may have been inspired by an idea of similarly blending or fusing his paint. That such a proceeding was indeed a part of the published methods (of which we were earlier unaware), suggests that Stubbs probably did make use of fusion of the wax-resin medium by heat as part of his process, at least in the case of the three panels not incorporating drying oil. The coincidence of Stubbs's interests in enamelling and in wax painting may also be related to the controversy concerning the methods of the Ancients. Some people apparently asserted that the much interpreted words of Pliny in fact referred to enamelling rather than a form of encaustic painting and Müntz [7] had devoted some space to refuting this.

Other eighteenth century artists, such as Reynolds, experimented with unconventional modifications of their painting medium but none seems to have adopted a changed technique so wholeheartedly as Stubbs. It is remarkable that his methods should have been so little known by his contemporaries or, if known, that they should have been so little commented on and subsequently so completely forgotten.

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Notes and references

1. WHITE, R., ROY, A., MILLS, J. and PLESTERS, J., 'Research Note. George Stubbs's "Lady and Gentleman in a Carriage": A Preliminary Note on the Technique', *National Gallery Technical Bulletin*, **4** (1980), p.64.
2. SHEPHERD, R., 'Stubbs: a Conservator's View', in *George Stubbs 1724-1806*, Tate Gallery Publications (London 1984), pp.20-21.
3. MILLS, J. and WHITE, R., 'Organic Mass-Spectrometry of Art Materials: Work in Progress', *National Gallery Technical Bulletin*, **6** (1982), pp.3-18.
4. WHITE, R., 'The Application of Gas-Chromatography to the Identification of Waxes', *Studies in Conservation*, **23** (1978), pp.57-68.
5. This figure is calculated from the results of TULLOCH, A. P., 'Beeswax: Structure of the Esters and their Component Hydroxy Acids and Diols', *Chem. Phys. Lipids*, **6** (1971), pp.235-65.
6. CAYLUS, le Comte de, and MAJALU, M., *Mémoire sur la Peinture à l'Encaustique et sur la Peinture à la Cire* (Geneva 1755).
7. MÜNTZ, J. H., *Encaustic: or Count Caylus's Method of Painting in the Manner of the Ancients* (London 1760).
8. FRATREL, J., *La Cire alliée avec l'Huile ou la Peinture à Huile-Cire. Trouvée à Manheim par M. Charles Baron de Taubenheim* (Mannheim 1770).
9. REQUEÑO, V., *Saggi sul Ristabilimento dell' Antica Arte de' Greci e Romani Pittori* (Parma 1784, 2nd ed. 1787), 2 vols.