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Thermomicroscopy applied to painting materials from the late 18th and 19th centuries

Joyce H. Townsend*

Conservation Department, Tate Gallery, Millbank, London SW1P 4RG, UK

Abstract

This paper discusses the application of thermomicroscopy in the temperature range 25–250°C for the characterisation of 100- and 200-year-old artists' paint. Studies of 20th century reference materials, and paint samples from Sir Joshua Reynolds (1723–1792), J.M.W. Turner (1775–1851) and J.A.M. Whistler (1834–1903) are discussed, to illustrate the utility of thermomicroscopy both for the materials analyst and for the paintings conservator. Turner's bituminous paint is prone to darken irreversibly at 75–88°C, while the 'megilp' formulations which he used are not distinguishable from oil paint with lead driers or oil with some resin added, though the group are distinguishable from unmodified oil medium. Beeswax and spermaceti wax melt out from Turner's paint formulations at the typical melting point for the wax, whereas Reynolds' paint formulations including beeswax have aged in a more complex way, and show melting point ranges which lie within those of the original components. Whistler's paints tends to darken irreversibly at 70–90°C due to the presence of additives in his manufactured tube paints, and their measured melting points indicate a complex ageing process which may be analogous to that in Reynolds' paint formulations.

Keywords: Thermomicroscopy; Artists' paint; Reynolds; Turner; Whistler

1. Introduction

Thermomicroscopy involves the simultaneous observation and controlled heating of small samples of material. It can be applied to small, layered samples such as those from easel paintings, where many paint samples are too complex for the dissection and detailed analysis of individual thin layers to be practicable. At its simplest, it yields information on the heat sensitivity of the paint. This is of great interest to the conservator planning treatments which might involve localised heating to re-attach paint flakes, or to correct out-of-plane deformations of the painting's surface. Paint softening, direct melting of components of the paint formulation, or irreversible darkening of the paint medium have to be considered in this context. These processes are of course the exception at the temperature range 50–70°C normally used to effect consolidation of the paint surface, but the exceptions tend to occur in paints of late 18th or 19th century, and sometimes in the work of specific artists. Sir Joshua Reynolds (1723–1792), J.M.W. Turner (1775–1851) and J.A.M. Whistler (1834–1903) are notable examples. Paintings by Reynolds and Turner frequently have damaged areas caused by softening or melting of paint during conservation treatments dating from the 19th century, while some late portraits by Whistler are today so dark, compared to paintings by his

* Tel.: +44-207-887-8072; fax: +44-207-887-8982.
E-mail address: joyce.townsend@tate.org.uk (J.H. Townsend).

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contemporaries, as to suggest that either his materials or otherwise safe conservation treatments have caused unusual damage here.

Thermomicroscopy can give valuable clues as to the ingredients used in paint formulations. It is useful in conjunction with other analytical studies, and with documentary studies concerning the materials available and likely to have been used by an artist, where it can be used to infer the likely composition of very small samples, or those contaminated by later conservation materials, both of which may be unsuitable for more detailed analysis.

Thermomicroscopy can be used as a means of predicting the likely discoloration of paint when it is heated, and therefore for assessing the likelihood that previous conservation treatments involving heat might have caused changes to the appearance of the works of particular artists. The 19th century practice of ‘lining’ a deteriorated canvas by attaching another canvas to it with glue-paste, using hot irons on the reverse, was such a treatments. It affected the whole image, some areas might have reached higher temperatures than others, and local heating to 90°C or more was possible. The assessment of heat damage depends on the discovery of paint never exposed to heat, for example that on a panel support, or, far better, from a surviving artist’s palette, an object unlikely ever to have been conserved, for study with thermomicroscopy. Heat-induced colour changes could be so widespread in the works of a particular artist today that the altered appearance comes to be regarded as almost normal for that artist.

2. Methods

Sub-milligram paint fragments were placed on a 0.17 mm glass coverslip on a 1.0 mm borosilicate glass microscope slide, placed on a Mettler FP82 hot stage linked to a Mettler FP80 processor. This provides linear, rate-controlled heating from 0.1 to 20°C/min to a temperature of 300°C, and the temperature measurement is claimed by the manufacturer to be accurate to ±0.8°C, or better. Heating rates of 5 or 10°C/min, over a temperature range 30–250°C, are suitable for many paint samples. Some, however, become so dark that no further changes can be seen, by 170°C. The sample can be observed in transmitted, polarised light with a binocular microscope at ×40–400 magnification, and photographed by maintaining the temperature of interest during exposure, rather than continuing heating. New paint fragments were used for repeat measurements, and paint not likely to have been heated in the past for studies on paint properties, lest thermal history should affect the behaviour of already-heated paint.

3. Thermomicroscopy applied to reference materials

Generally, softening (or slight slumping) of any sample can be seen at these magnifications, 5–10°C below the temperature at which it is completely melted. With waxes, there is often a smaller range 2–3°C between the first onset of melting, and the completely liquid state, and cooling samples re-solidify over the same range.

The glass transition of most paints, and many varnish materials, lies well below their melting point, and 15–20°C above a room temperature of 20°C [1]. Schilling [2] has measured T_a, T_b and T_c for natural and synthetic resins on first and second heating, and found glass transitions (T_c) of natural resins such as dammar, mastic, shellac and sandarac in the range 54–66°C. These materials have an ill-defined average molecular weight (they are highly polydispersive) and considerable variability in properties, since they come from a variety of botanical sources. They possess a melting point range, rather than a sharp melting point. Synthetic picture varnishes in regular use have lower values for T_c [2]: 37–41°C for Paraloid B-72 (ethyl methacrylate/methyl acrylate copolymer), 43–54°C for Laropal K-80 (polycyclohexanone) and 49–57°C for MS2A (reduced polycyclohexanone), and much sharper melting points, which reflect their better-defined molecular weight range.

Published melting points [3–5], obtained from several sources, for materials used in the late 18th and 19th centuries are listed in Table 1. Measurements by thermomicroscopy on actual materials are listed in Table 2. Where possible, old material of known composition was selected for measurement, to simulate the naturally aged components of paintings. There is good agreement between published and measured results.

Table 1
Published melting points for waxes and tallows

Material	MP (°C)
Beeswax [3]	62–65
Beeswax [4]	63
Beeswax, crude [5]	62–68
Beeswax, yellow [5]	61–69
Carnauba wax [4]	84
Carnauba wax [5]	83–86
Mutton tallow [5]	42?
Shellac wax [5]	79–82
Spermaceti wax [5]	42–50
Wool wax [5]	36–43
Natural resins, e.g. mastic, dammar, rosin [5]	<120

4. Measurements on artists' paint samples

In this study of 100- to 200-year-old paints, unmodified linseed oil paint always began to darken at 120–140°C without melting, while egg and glue samples began to darken at 180–200°C, but did not melt. This matches published findings on 400-year-old paint [6].

Bituminous paint began to darken at 75–88°C in different samples, and darkened rather rapidly thereafter until no further change was visible in this naturally dark brown material. This finding has not been previously reported in the conservation literature, but is supported by the very darkened appearance of bitumen-rich areas in Turner's lined easel paintings [7].

Natural resin varnishes, resinous glazes and 'megilps' have a component which melts out at 110–120°C, and the last group tends to darken at 120–130°C. This agrees with the melting point measured for mastic resin, and is consistent with known 19th century usage of materials: mastic varnish, made by dissolving the resin in an alcohol or in oil of turpentine, was often used as a picture varnish, while dammar was probably not available in UK until mid-century [8], and did not win instant popularity even then. Recent analyses of varnishes applied in the 19th century and early 20th century have found predominantly mastic resin [9]. The 'megilps' mentioned above are formulated from linseed oil prepared with a lead drier, and mastic varnish prepared in oil of turpentine, in a proportion of 1:1 or 1:2 oil:resin. Their second-order transitions as measured by TMA, and other analytical studies, support a distinction between 'resinous glazes' which include mastic resin but are still oil-rich, and megilped material, which always includes a phase with distinct properties from the oil or resin alone [10]. Thermomicroscopy, however, cannot distinguish them: in both cases melting occurs at 114–120°C as mastic resin is freed, while the oil polymer network begins to darken at about 130°C. Nor could it indicate differences between unmodified oil, and oil prepared with a lead drier, when found in paint of this age.

Observations during thermomicroscopy of a few samples of Turner's paint have already been published in this journal, with micrographs to illustrate the different stages in heating [11]. For example, a brown glaze removed from Turner's The Opening of the Walhalla, 1842 (Tate Gallery N00533, exhibited 1843), a painting with a variety of modified oil media applied to a primed hardwood panel, and little history

Table 2
Softening and melting points of artists' materials in the Tate Gallery conservation archive, measured by thermomicroscopy

Material	Source	Softening (°C)	Melting (°C)
Beeswax	1961 commercial source	54	59–62
Shellac wax, bleached	1990 ditto	73	80–83
Synthetic spermaceti wax	1990 commercial source	40	42–44
Genuine spermaceti wax	FOM-AMOLF, Amsterdam, 1990s	40	42–44
Dammar resin	Early 1950s commercial source	97	100–104
Mastic resin	Early 1950s ditto	112	115–120
Rosin	1980s ditto	96	100–103
Sandarac	Early 1950s ditto	114	125–135
Copal	Early 1950s ditto	90	99–102
Paraloid B-72 picture varnish	Manufacturer, late 1980s	103	113–117
Stearates added to tube paints	Various	65–70	70–75

of conservation treatments involving the application of heat in the past, showed firstly partial melting between 30 and 55°C. Spermaceti wax, which melts at 42–44°C, was analysed in an adjacent sample by means of direct temperature-resolved mass spectrometry [12]. Partial melting within the 110–120°C melting range for mastic resin, darkening of one component between 131 and 181°C, and darkening of another component thereafter were also observed. DSC [11,13] and DTMS [12] of this paint confirmed that it included proteinaceous material as well as oil, as would be predicted from these melting ranges.

Thermomicroscopy offers the advantage that the layer which contains a material of low melting point can be localised. Beeswax coatings applied to matt down a natural resin varnish can be seen to melt out from the varnish surface, which is of little concern if that varnish will be removed before localised heat treatments would be applied. Waxes melting out from the paint medium can also be recognised. Turner's paintings quite often include a paint formulation of unrefined beeswax and linseed oil, analysed by GC-MS in samples from The Opening of the Walhalla, 1842 [7], and this has a melting range 56–60°C. It can just be distinguished by thermomicroscopy from the beeswax and mastic resin lining mixture used for many of Turner's canvas paintings, which has a melting range 60–64°C, if several tiny samples from different areas are available for comparison.

Brown paint in the background of Reynolds' Self-Portrait as a Doctor (Tate Gallery N00306 c.1775, canvas lined at least once) which softened at 114°C and was fully melted by 135°C was found by DTMS to include mastic resin and possibly bitumen as well as linseed oil. Red paint which included vermilion and unmodified walnut oil, from Reynolds' Self-Portrait as a Deaf Man (Tate Gallery N04505 c.1775, canvas lined at least once) did not darken until it reached 140°C, which is comparable behaviour to unmodified linseed oil. The later George IV when Prince of Wales (Fig. 1, Tate Gallery N00890, 1785, panel support not heat-treated) is painted entirely in a formulation which comprises beeswax and mastic resin with traces of linseed oil detected in some samples with DTMS. These analyses are described in greater detail elsewhere [14,15]. This formulation, consistent with later 18th century published recipes on the preparation of a wax medium to be used at room temperature [16], is distinct from Turner's resin-free wax paint, which had melting points corresponding to its ingredients. Reynolds' formulation consists mainly of easily oxidised and hydrolysed components, and they have interacted to give a paint which melts completely in the range 77–95°C for different samples with varied proportions of beeswax. This lies between the melting ranges of the two components.

A palette belonging to Reynolds, and a canvas which he used for experimental purposes, were also available for analysis. The latter is complicated by three coats of mastic-type varnish applied later. Several of these samples include a component which melts out readily at 61°C, which can be attributed to beeswax, by comparison with DTMS results [17]. The sample labelled in Reynolds' hand "Prussian blue cer" ("cera" is Italian for wax) was found to consist purely of beeswax when it was analysed with DTMS, and it melted completely at 61°C. Others had a component melting at 66–68°C, or at 90–91°C, and a preliminary interpretation suggests that beeswax degradation products may be responsible. The samples which did not show melting until 110–114°C correlated well with the finding of mastic resin as well as an oil polymer network. The identity of a component which melts at 130–140°C remains unknown.

Paint from Whistler's nocturnes, and paint from a palette which he used, has also been examined with thermomicroscopy, and analysed with DTMS and GC-MS in a few cases [18]. These would have been commercially produced tube paints, in contrast to those used by Reynolds and Turner. Most of the paint, except for white samples, yellow ochre, sienna and ochres, darkened at 70–90°C. The exceptions probably have a medium of unmodified oil, analysed as walnut or poppyseed oil for the white paint. The red paint, and medium-rich samples where Whistler had added his so-called "sauce" of stand oil, mastic resin and lead drier [18] had components which melted at 58–61, 70 and 100°C. Some of these samples melted completely at 70°C, which makes the inference untenable that stearates added by the manufacturer account for this melting range, because they would always be a minority component. Beeswax was detected by DTMS in some samples, hence the melting at 58–61°C can be attributed to this component, which

Fig. 1. George IV when Prince of Wales (Tate Gallery N00890, 1785, panel support 756 mm×616 mm).

would also have been a manufacturer's additive. (This follows from its detected presence in tube paint squeezed straight onto the palette, and not modified by the artist.) There may be an analogy here with the anomalous melting points (one was approximately 70°C) of Reynolds' beeswax/mastic paint formulation, and the paint on his experimental canvas. They too were severely discoloured. If the ageing process of tube paints with additives is even more complex than that of unmodified oil paints, as seems likely, the unusual heat sensitivity compared to additive-free paint, and ready formation of yellow compounds, may eventually be explainable. Such ageing processes are currently being investigated [19,20].

5. Conclusion

Thermomicroscopy of very small paint samples weighing approximately 100 μg can yield valuable information on the heat sensitivity of paint for the conservator planning a conservation treatment which might involve heat. It can also give clues as to paint composition. At worst, it may indicate which components are more and less relevant for further analysis when the sample size is limited, and at best, when carried out in conjunction with a study which involves detailed analysis of many paint samples, it can be used to predict composition in areas of a painting which are too complex, or too contaminated by conservation materials, for meaningful chemical analysis. Information on the likelihood that the paint has darkened due to lining or other treatments involving heat can also be gained from such a study, when never-heated paint is available for comparison. Improved understanding of the chemistry of modified oil paint may make it possible to infer more detailed information from thermomicroscopy.

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