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PRELIMINARY INVESTIGATIONS OF THE BINDING MEDIA OF PAINTINGS BY DIFFERENTIAL THERMAL ANALYSIS

*M. Odlyha and **A. Burmester

* SCHOOL OF CHEMICAL TECHNOLOGY, SOUTH AUSTRALIAN INSTITUTE OF TECHNOLOGY, P. O. BOX 1, INGLE FARM 5098, SOUTH AUSTRALIA
** DOERNER-INSTITUTE, BARER STR. 29, 8000 MUNICH 40, WEST GERMANY

Differential thermal analysis has been used to study the binding media of paintings. To assist in the interpretation of the DTA curves known organic materials which are commonly used in paintings such as linseed oil, egg yolk and their mixtures with pigment (e.g. linseed oil/egg yolk/ZnO) were initially investigated together with paint films containing linseed oil/lead white and some additions of proteinaceous material. The paint films had been prepared in the period 1915–1941. It appears as though DTA or DSC can be used both to characterize the binding media (i.e. to decide whether oil or protein appears as the main component), and to provide an indication of the age of the painting.

A recent article draws attention to the number of techniques which have been used to study paint media [1]. Previous work using differential thermal analysis [2] (DTA) is also mentioned, though with a degree of caution, for according to the author it seems difficult to reproduce and the suggestion is made that further experiments be carried out to evaluate the influence of additives such as pigments or other binding media.

The results of the previous work can be summarized as follows:

- two exothermic reactions were observed on heating the oil-based media in oxygen, the first reaction occurred in the region of 250–300°, the second reaction occurred in the region of 400°,
- the ratio of peak heights (i.e. high temperature peak to low temperature peak) of the two reactions varied linearly with the logarithm of the age of the painting. This provided the possibility of dating oil paintings up to 100 years old with an error range of ± 15 years, and of determining recent forgeries,
- where the paint sample was more than 150 years old mainly the reaction at 400° was observed, where it was more recent then the reaction at 300° dominated.

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The aim of the project was to assess the overall suitability of DTA (or DSC) for the study of the binding media of paintings, and in so doing (1) to attempt to determine whether the effect of additives such as pigments or the presence of other binding media in a paint sample can be observed by DTA (2) and then to check the previous claim that the variation in thermal behaviour with the age of the paint samples could be used to date oil paintings up to 100 years old.

Experimental procedure

Samples in the range 0.1–0.4 mg were heated at 5 deg min^{-1} in the Mettler TA 2000B instrument as in the previous work. The heating was carried out in all cases in an atmosphere of pure O_2 (flow rate ca. 40cm^3 min^{-4}) and to a maximum temperature of 500–550°. The samples were heated in Al crucibles and an empty crucible was used as the reference.

Paintings: the medium

The structure of a painting can be simply described as a series of paint layers on a prepared surface (the ground) over a support of canvas or wood. The paint layers essentially consist of two components: the pigment and the medium. The role of the medium is to bind the pigment particles together and to make them adhere to the prepared surface. Materials which have used for the medium include substances such as egg yolk, plant gums, drying oils, waxes and resins. They can be considered as natural polymers, for proteins (e.g. egg yolk, rabbit skin glue) are condensation polymers of amino acids, plant gums (e.g. gum arabic) are polysaccharides or condensation polymers of the monosaccharides, and drying oils (e.g. linseed oil) contain triglycerides with a large proportion of polyunsaturated fatty acids which enhance oxidation and polymerisation processes essential for film formation.

Paintings: the drying process

To function in a satisfactory manner the medium must dry to form a hard film of embedded pigment particles. In the case of drying oils chemical changes occur namely oxidation and polymerization [3]. In the case of proteinaceous materials the changes, apart from the initial loss of water, are not so well understood. According to Karpowicz [4] this may be due to the exceptional stability of proteinaceous media in comparison with the more rapid deterioration of aged oil and resins.

The drying process in oil-based media depends on the film thickness and on the nature of the pigments present e.g. a pigment such as lead white is known to accelerate the drying process. This does not mean, however, that lead white accelerates degradation processes. Recent studies have shown that it inhibits photo-oxidation of paint layers in contrast to e.g. vermilion which accelerates it [5].

The drying process can be accelerated by boiling, e.g. linseed oil in the presence of small amounts of siccative (e.g. PbO). This method has been used to prepare oil varnishes. In the process of boiling the oil becomes partly oxidized and polymerized and so dries more rapidly than the untreated oils. Hence the particular use as varnishes for paintings.

In view of the polymeric nature of the materials to be investigated and the oxidative degradation processes which occur it seems appropriate to use DTA for the study of paint media particularly since it has been used successfully to characterize a number of polymer blends, to demonstrate the effects of ageing and the presence of additives, and to identify elastomers on the basis of their thermooxidative degradation characteristics [6].

Samples investigated by DTA

Samples investigated by DTA included:—

A. Known pure organic materials which are commonly used as binding media in art works and their mixtures both with and without pigment [e.g. linseed oil/egg yolk (1:1) + ZnO]. These samples had been prepared as films on glass slides in 1983 and had aged under normal conditions in the laboratory [7].

B. Accurately dated paint films prepared during the period 1915–1941 on canvas or board and containing linseed oil/lead-white pigment (or ZnO or TiO_2) together with known additives (resin mastic, egg yolk) [8].

C. 41 accurately dated and signed paintings ranging from early Italian (13th-17th century) [9] to later German (early 19th–20th century) [10].

Sampling

It is commonly accepted that as soon as a painting is finished it starts to deteriorate [11]. Samples from actual paintings can therefore be considered as partially degraded or aged samples since natural ageing processes alter the initial properties of the paint media.

In view of the factors affecting samples from a painting it was decided to select them in a way which would minimise their differences. Thus samples were removed only from areas containing white pigment. The decision to choose white areas was based mainly on the fact that fewer pigments are present there. In the previous work there does not appear to be any strict adherence to colour though brief mention is made of the fact that the best results were obtained from dark-coloured samples, and that the effect of pigments on age-related changes in the DTA curves was still to be explored.

A precise sampling procedure was also observed which was based on the previous study of paintings by DTA. Samples were taken from the top layer only, after the varnish had been removed. It was necessary to restrict sampling to the top layer to avoid effects caused by an ageing gradient. It was also necessary to avoid areas of restoration, and to make sure that no ground layer adhered to the sample as this was shown in the previous study to have a direct effect on the shape of the DTA curve.

Results

A: DTA curves of the known organic materials showed on the whole a two peak exothermic pattern in the 200–520° region. The peak temperatures, the relative sizes of the peaks and the peak shape showed sufficient variation so that the complete combustion curves could be used to characterise the substances and act as "fingerprints", Figure 1, curves (1) to (5) [12].

Effects due to polymerisation and the presence of additives were also observed. A sample of boiled linseed oil where some oxidation and polymerisation had occurred in relation to the raw oil sample gave a DTA curve which differed significantly from that of raw oil. The intensity of the first peak had been reduced and that of the second peak had increased. (Figure 1, curves (3) and (4)).

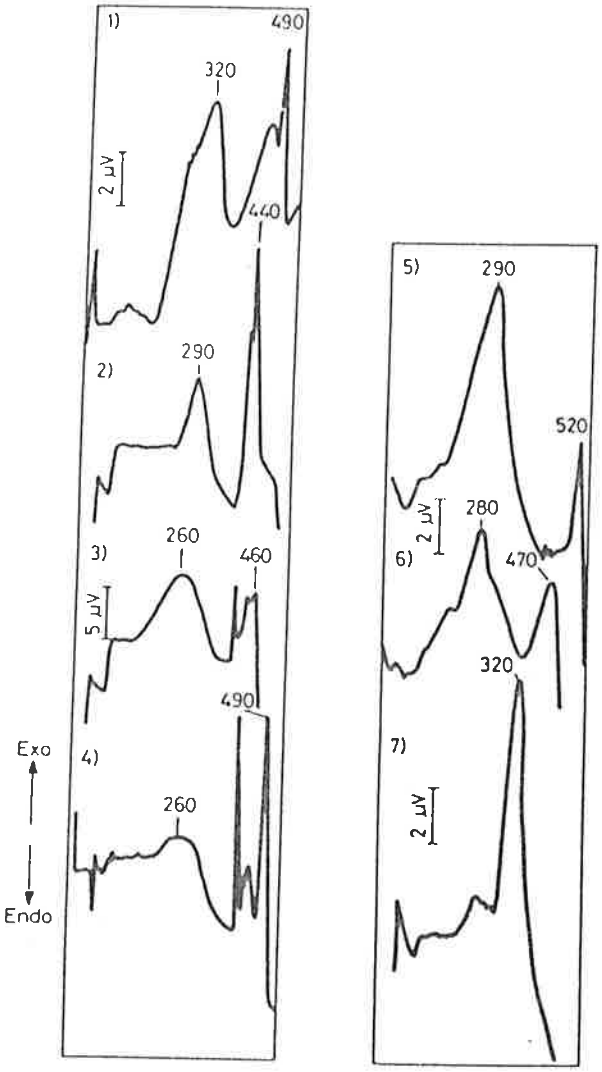

Fig. 1 DTA curves of known organic materials (1) Rabbit skin glue, (2) Gum arabic, (3) Raw linseed oil, (4) Boiled linseed oil, (5) Egg yolk, (6) Egg yolk/resin mastic (1:2) (7) Egg yolk/resin mastic (1:2) + ZnO

B: DTA curves of old pigmented films (1915–1941) containing lead white and linseed oil showed also a two peak exothermic system, this time in the 200–380° region.

The relative sizes of the peaks appeared to vary with the age of the sample, the presence of additives, and any pre-treatment of oil such as bleaching (Figure 2, curves (1) to (5)).

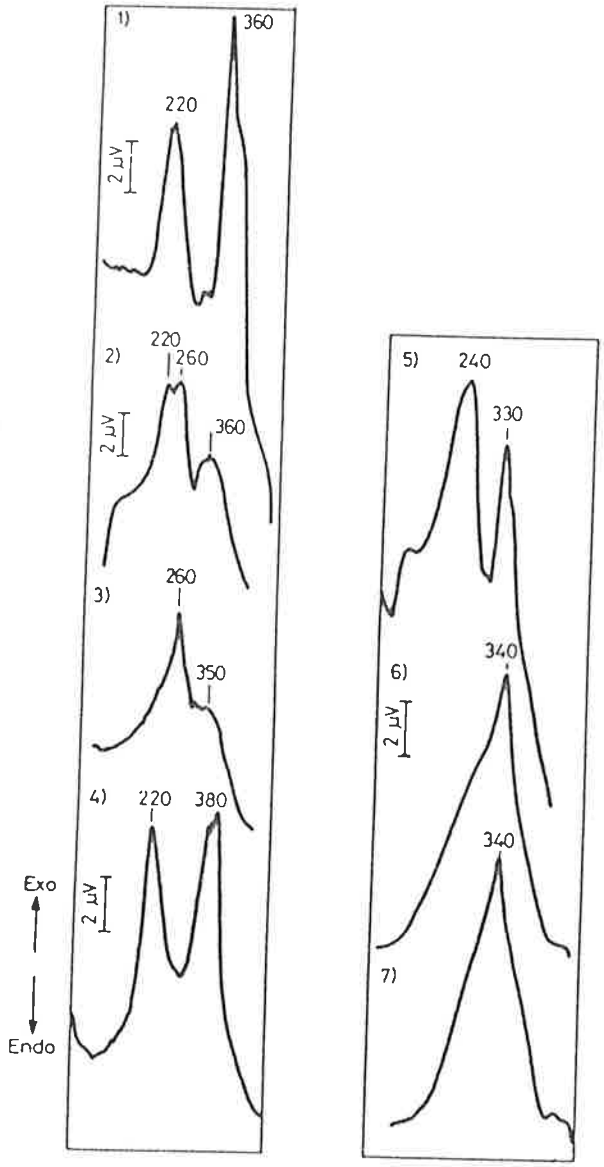

Fig. 2 DTA curves of prepared paint films (1) Lead white/linseed oil 1915, (2) Lead white (oil) egg tempera 1925, (3) Lead white/egg tempera 1943, (4) Lead white/linseed oil (bleached) 1917, (5) Lead white/linseed oil (raw) 1941, (6) ZnO/Oil 1941, (7) Titanium dioxide/linseed oil 1940

In the case of the oil/egg tempera/lead white sample it was interesting to observe that the effect of the egg tempera was to suppress the second high temperature exotherm in oil. (Figure 2, curve (2)). This effect has been observed in the study of plant material where the presence of components with high nitrogen content (proteins) cause the termination of the second exothermic step at higher temperature [13].

The effect of different white pigments (lead white, ZnO, and TiO_2) on the drying of linseed oil can be seen in Figure 2, curves (5), (6) and (7). The white pigments alone were also heated in oxygen. Their DTA curves showed no definite characteristics.

C: Most of the samples taken from areas containing lead white (pigment determination was carried out by optical emission spectroscopy and X-ray diffraction) behaved in a similar manner to the prepared paint films containing lead white and linseed oil in that two exothermic reactions in the region 200–380° were observed (Figure 3, curves (1) to (3)). It is interesting to note that interpretation of data from paint media poses similar difficulties to those encountered with biological materials since both systems can be aptly described as "multi-component, molecularly non-homogeneous material in which part of the components exist (sic) as continuous, separate and intermingling structures" [14].

A ratio (Q) of peak heights (height of high temperature exotherm/height of low temperature exotherm) was calculated and plotted against the logarithm of the age of the paintings (Figure 4) as in the previous study. The following observations were made:–

(1) Paintings of about 300–450 years exhibited a peak ratio which was similar in nearly all cases investigated. In Figure 4 this value is designated by the cluster labelled *h*. A DTA curve of such a painting appears in Figure 3, curve (4).

An exception did occur in paintings of this age. The DTA curve of a sample from a 13th century painting by Coppo di Marcovaldo showed a dominant peak in the lower temperature region (250°), Figure 3, curve (5), and differed markedly from a sample (16th century) which gave what could be designated as the "oil DTA curve", Figure 3, curve (4).

Microchemical tests also indicated the presence of proteinaceous medium and art historical information would confirm this result since the technique of painting in oils in Italy had not yet been introduced.

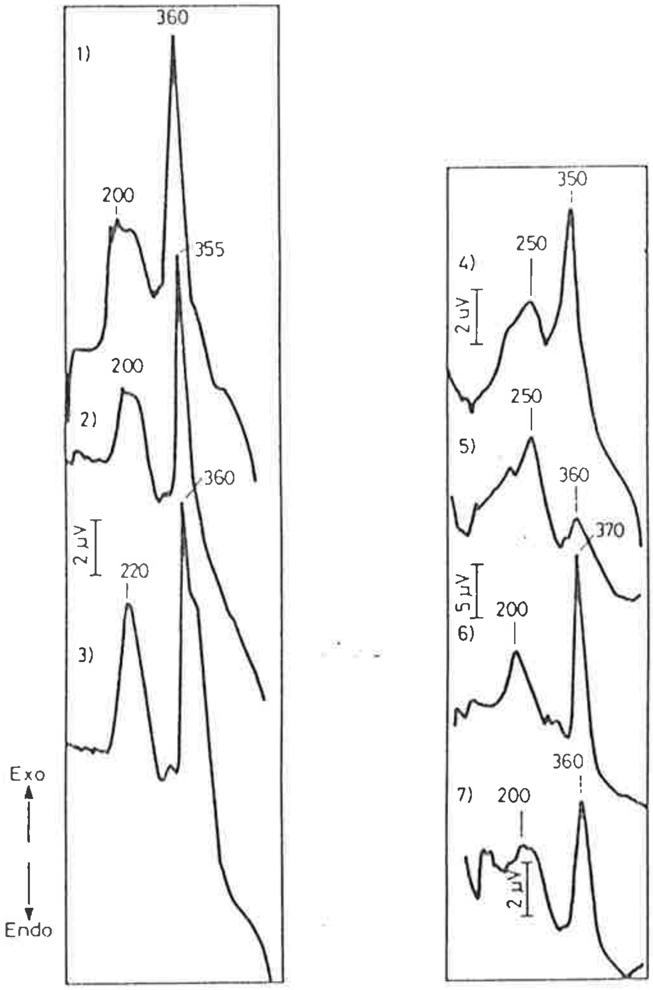

Fig. 3 DTA curves of samples from paintings. (1) O. Strützel, "Eichen in Landschaft" (No. 8876), 1890 (2) T. Weber, "Ströbing bei Endorf" (No. 11073), 1909, (3) Prepared paint film, lead white/linseed oil 1915, (4) L'Ortonlano, Museo di San Martino Napoli, 1521 (5) Coppo di Marcovaldo, "Madonna del popolo" Capelle Branacci, Chiesa Carmina, Florence – 13th century, (6) M. Feldbauer, "Frauenakt" (No. 10247), 1906, (7) K. Seiler, "Offizier in Dienst" (No. 13939), 1904.

The DTA curve from such a sample could in future be used as a standard curve for old proteinaceous material and lead white pigment. There is always the problem in this field of study of obtaining samples which can accurately represent the age-induced changes in paintings over 100 years old.

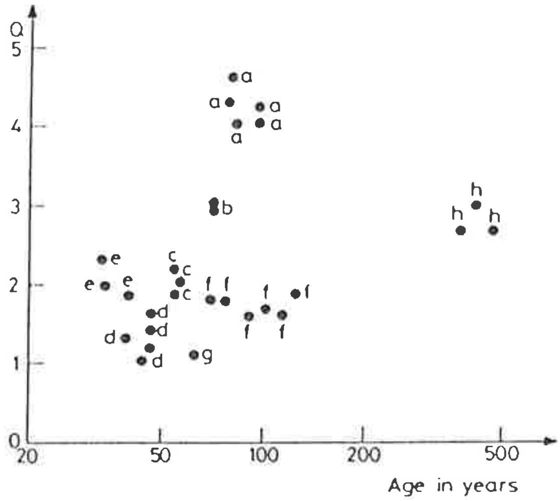

Fig. 4. a) Paintings 1890–1909, b) Paint films (lead white/linseed oil 1915) c) Paintings 1926–1932, d) Paint films (lead white/linseed oil 1941) (2 paintings 1943–1948), (e) Paintings 1947–1954 (ZnO/TiO_2 pigments), f) Paintings 1862–1910), g) Paint film oil/egg tempera/lead white 1925, h) Paintings 1521/1560.

(2) Paintings of the late 19th to early 20th century (1890–1909) exhibited a peak ratio which was similar only in some of the samples investigated. The value is designated by the cluster labelled *a*. The corresponding DTA curves appear in Figure 3, curves (1), (2), (6) and (7). Other samples from this period gave another peak ratio value which is represented by the cluster *f*.

(3) Paintings from 1926–1932 gave a peak ratio value represented by the cluster labelled *c*.

(4) Prepared paint films containing lead white and linseed oil from 1915 and 1941 gave peak ratios which are described by the clusters *b* and *d* respectively. Corresponding DTA curves are shown in Figure 2, curves (1) and (5). The region *d* contains also two values for peak ratios from paintings of the period 1943–1948.

(5) Paintings from 1947–1954 gave a peak ratio value represented by the cluster labelled *e*. This is the only group where the white pigment is not lead white but either ZnO or TiO_2.

(6) A prepared paint film containing oil/egg tempera/lead white (1925) gave a peak ratio described by the point *g* (DTA curve, Figure 2. curve (2)). This appears in the neighbourhood of cluster

f (refer to (2) above). It may be that the samples in this group *f* contain mixed media (oil/protein). Other tests (e.g. microchemistry) would need to be carried out to verify this observation.

Thus results indicate the changing values of Q with age and with medium type (the peak ratio labelled *g* represents this effect). Further samples need to be studied, however, to define these trends more clearly. As far as the previous work is concerned the following similarities and differences were observed:

- two exothermic reactions did occur on heating oil-based media in oxygen. However, the temperature range of the two reactions differed slightly – the first reaction occurred in the region 200–250° (cf. 250–300°); the second reaction occurred in the region 340–380° (cf. 400°);
- the ratio of peak heights (Q) did vary with the logarithm of the age of the painting. However, the scatter in the Q values in the present data seems to point to clusters of values from samples of similar age, medium and pigment rather than to a linear relationship as proposed in the previous study. It is interesting to note that though a linear relationship was proposed in the previous work the two graphs are not consistent. Significant differences in peak ratios are found for a given age of painting. [2, 15]
- in paint samples more than 150 years old (e.g. 470 years, Figure 3, curve (4)) two reactions were still observed for oil-based media. The reaction at 400° did not solely dominate as described in the previous work. The latter effect was observed, however, in prepared paint films containing oil and resin or for varnishes (probably oil-resin) from paintings.

Conclusions

It appears as though DTA can be used for the study of the binding media of paintings.

(1) It is sensitive to the presence of additives in the known organic materials tested from 1983.

(2) It has also shown that it can detect the presence of mixed media in older samples in the region of 50–60 years old.

(3) It seems possible to distinguish between non-oil and oil-based paint media even in samples which are about 500 years old.

(4) The 2-peak exothermic pattern (200–380°) which recurs for linseed oil/lead white mixtures has possibly provided a means for characterising oil-based paint media.

(5) The variation in the peak ratios (Q) at this stage seems to provide an indication of age-induced changes rather than a dating test.

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References

1 L. Masschelein-Kleiner, "Analysis of paint media, varnishes and adhesives," PACT-Strasbourg, 13 (1986) p. 203.

2 F. Preußer, Thermal Anal. 16 (1979) 277–283.

3 J. S. Mills, Gas Chromatographic Examination of Paint Media, Part 1. Fatty Acid Composition and Identification of Dried Oil Films, Studies in Conservation, 11 (1966) 107.

4 A. Karpowicz, Ageing and Deterioration of Proteinaceous Media, Studies in Conservation, 26 (1981) 153–160.

5 F. Rasti and G. Scott, The effects of some Common Pigments on the Photooxidation of Linseed Oil-based Paint Media, Studies in Conservation 25 (1980) 145–156.

6 E. A. Turi, Thermal Characterization of Polymeric Materials, 1981, Academic Press, London, p. 584.

7 Samples were provided by Dr. Matteini of the scientific department for the examination of works of art at the Fortezza da Basso in Florence.

8 Samples belong to the Doerner Institute in Munich.

9 Samples were obtained from the Restoration laboratories at the Fortezza da Basso, Florence.

10 Paintings sampled belong to the Bavarian State Paintings Collection.

11 H. Ruheman, The Cleaning of Paintings, 1968 Faber and Faber, London.

12 Poster of this work was presented at the European Symposium on Polymer Blends in Strasbourg, May 25–27, 1987.

13 E. M. Varju, Some Studies of the Dry-Ashing Sample Preparation Method of Plant Material by Thermoanalytical Procedure, in Thermal Analysis, Vol. 2, Proceedings of the 4th ICTA, Budapest, 1974, p. 245.

14 R. C. Mackenzie, Differential Thermal Analysis, Vol. 1, 1970, Academic Press, London.

15 F. Preußer, Differentialthermoanalyse-eine neue Methode zur Gemäldeuntersuchung, Maltechnik Restauro, 85 (1979) 54–60.