Thermochimica Acta, 134 (1988) 85–90
Elsevier Science Publishers B.V., Amsterdam

CHARACTERISATION OF AGED PAINT FILMS BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Oxidative degradation studies of aged paint films by DSC have revealed that it is possible to distinguish between linseed, walnut, and poppyseed oils. This is of particular interest for several reasons:- the oil type can provide information on the provenance of a painting; the observed difference can assist in the interpretation of data relating to the study of the ageing properties of paint media by DSC. Two exothermic reactions occur in the range 30-500C. The intensity of the second exotherm decreases in the order linseed oil>walnut oil>poppyseed oil which corresponds to the rate of drying of the oils and is directly related to the linolenate content.

INTRODUCTION

Earliest studies of the effect of heat on paint films were carried out by Eibner on films up to 10 years old. He found that the best possible way of distinguishing between linseed and poppyseed oils was to observe the behaviour of these films on heating.[1] The aim of this study was to determine whether differences between the various drying oils linseed, poppyseed and walnut in the dried state and mixed with the pigment basic lead carbonate could be observed using DSC. The mixture of white lead pigment and drying oil was chosen since it commonly occurs in old paintings.

The use of linseed and walnut oils in paintings is well documented from the 14th century.[2] In Italy walnut oil was mainly used up to 1500 whereas in northern European countries the faster drying linseed oil was preferred. Poppyseed oil was introduced at a later stage in the 17th century. Its main disadvantage is its slow drying rate which can be attributed to the fact that it has no linolenic acid or linolenates to promote this action. This is in contrast to both linseed and walnut oils which contain 52% and 12% respectively.[3] It has been reported that yellowing and other film properties such as rates of drying are influenced by linolenate content.[4]

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

The present method for characterising the drying oils uses GC/MS and is based on the determination of the ratio of Palmitic to Stearic acids (P/S) in the triglycerides of the oils. These ratios have particular values and are stable.[5] It appears, however, that fats can also be characterised by P/S ratios which are similar to those found in drying oils. Therefore it would seem appropriate to look for additional methods such as DSC for characterising the drying oils.

EXPERIMENTAL PROCEDURE

Paint samples, typically 0.2(±0.01)mg, were weighed on a microbalance in Aluminium pans and then heated at 20C/min in the Perkin Elmer DSC7 system. Oxygen was used as the purge gas with a flow rate of about 40cm3/min. Samples were heated in open crucibles and an empty crucible was used as the reference. Samples were obtained from paint films provided by the National Gallery Scientific Department in London.[7] They had been prepared by spreading each oil/pigment mixture in duplicate on glass plates and then aged in the light above one of the exhibition galleries. For the DSC investigations samples were taken from the surface to avoid effects caused by an ageing gradient.

RESULTS

The DSC curves of samples from the three test films showed a similar pattern in all cases and one which has been observed in previous investigations of old pigmented films (1915-1941) containing lead white and linseed oil.[8] However, sufficient differences exist within this pattern to define each of these films. The main distinguishing feature is the size of the second exothermic peak (Table 1) and the subsequent peak ratios obtained from the two peak heights (Table 2). Linseed oil differs most significantly from the other two oils in that its second exothermic peak is about twice the size of the corresponding peak in the other two oils (Diag. 1). This same peak in walnut oil is slightly greater than in poppy oil, and poppy oil shows a more pronounced shoulder which is reproducible (Diag. 2).

As far as the first peak is concerned this occurs in all three cases over a broad temperature range. The peak areas decrease in order linseed> poppyseed>walnut, and the peak maximum for linseed oil occurs at a slightly higher temperature. Calculated peak ratios for the three pigmented films reveal that linseed oil(4-5)>walnut oil(2.3-3.2)>poppyseed oil(1.6-2). Peak ratios were calculated from the respective heights of the high and low temperature exotherms.

TABLE 1:

Characteristic features of DSC curves of oils.

PEAK 1			
Sample	Onset temp. (°C)	Peak temp. (°C)	Peak height(W/g)
Linseed oil	192	254	4.9
	181	245	4.2
	185	241	4.2
	187	235	4.6
	188	249	4.8
Walnut oil	191	229	3.6
	195	236	3.5
	192	227	3.3
	186	229	4.2
	187	232	4.2
Poppyseed oil	195	230	5.1
	189	227	4.3
	201	228	4.6
	188	230	4.3
	189	229	4.7
PEAK 2			
Sample			
Linseed oil	391	426	23.9
	408	421	19.2
	377	424	21.6
	372	426	18.9
	386	424	20.4
Walnut oil	348	420	11.5
	351	421	10.9
	369	420	10.0
	373	421	10.5
	354	420	9.7
Poppyseed oil	357	419	8.8
	356	417	8.1
	354	416	9.3
	354	417	8.0
	356	416	7.6

TABLE 2:
Ratios between intensities of peak 1 and those of peak 2.

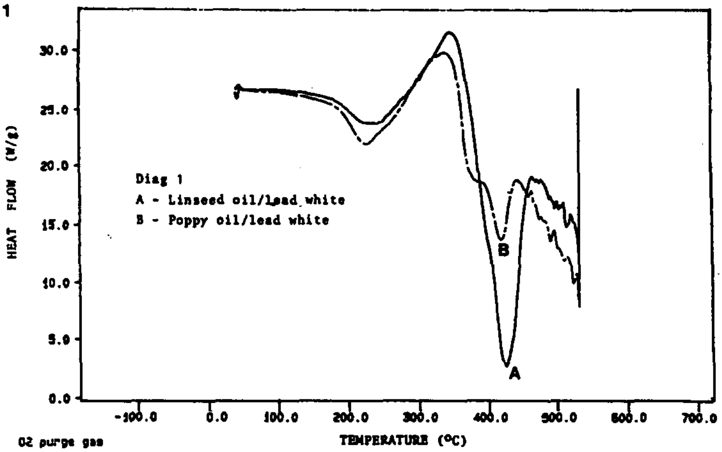
Sample	Peak ratio
Linseed oil	4.8
	4.6
	5.1
	4.1
	4.3
Walnut oil	3.2
	3.1
	3.0
	2.5
	2.3
Poppyseed oil	1.7
	1.9
	2.0
	1.9
	1.6

Results shown in Tables 1 and 2 represent independent measurements made on 5 different samples taken from the 3 standard paint films provided. There is a reasonable degree of reproducibility both in the calculated parameters such as onset temperature, peak temperature, and peak height, and in the shape of the actual DSC curves obtained. Diagram 3 show two DSC curves which were obtained from independent measurements made on two different walnut samples.

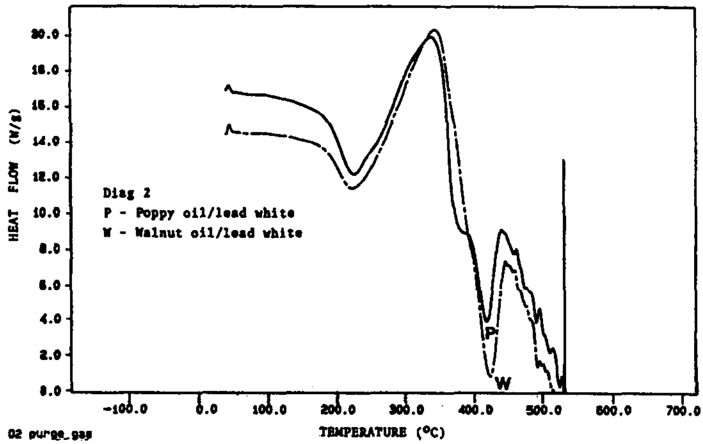
CONCLUSIONS

It appears as though DSC can be used to distinguish between the three drying oils even in paint films which have been aged so that they correspond to samples several hundred years old. This has been estimated on the basis of their sterol composition.[9] The peak ratios obtained vary in a manner which is related to the rate of drying of the oils - linseed>walnut>poppyseed and to initial proportion of linolenate present which clearly influences the extent of degradation of the oils.

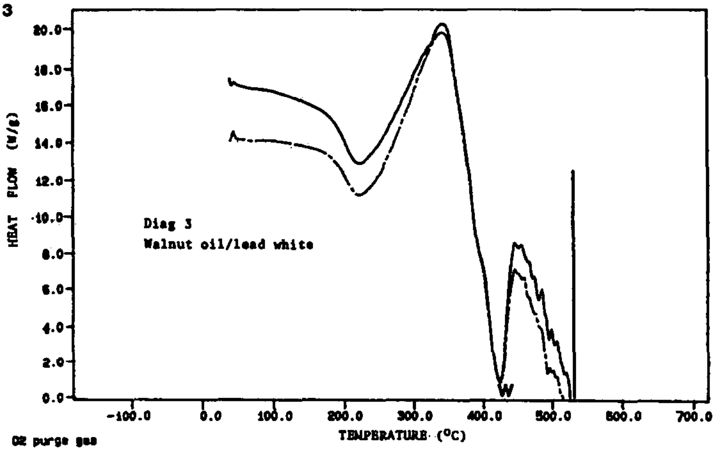
DIAG 1



DIAG 2



DIAG 3



g. 1: DSC curves of drying oils.

The two exothermic reactions can be interpreted as the combustion of in the first instance materials rich in oxygen (e.g. azelate-ester of the C9 dicarboxylic acid which forms as an oxidation product during drying of the paint films[10]) followed by the combustion at a higher temperature of polymerized, highly cross-linked materials which form by means of a free radical chain reaction and contain a larger proportion of carbon-carbon linkages[11]

ACKNOWLEDGEMENTS

Thanks are directed to Professor C D Flint for providing me with the opportunity of carrying out this work on the DSC7 system at Birkbeck College.

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