Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 237–239

# A DSC STUDY OF THE EFFECT OF LEAD PIGMENTS ON THE DRYING OF COLD PRESSED LINSEED OIL

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Cold pressed linseed oil and paints prepared using the inorganic pigments; lead white and red lead, were characterised using non-isothermal differential scanning calorimetry (DSC) in an air atmosphere to determine the effect of the pigment on the oxidative polymerisation of the drying oil medium. For each paint sample, the onset temperature for oxidation was reduced from 166°C to the range 50 to 60°C when a heating rate of 5 K $min^{-1}$ was used. In order to determine the rate of drying, the non-isothermal experiments were carried out using a range of heating rates. A change in the mechanism oxidative polymerisation was observed as the heating rate was increased.

***Keywords:*** *drying oil, DSC, lead white, linseed oil, red lead*

## Introduction

Cold pressed linseed oil (CPLO) is one of the many drying oils used by artists in the preparation of pigmented paints. It is an example of a naturally derived seed oil based on a triglyceride structure. The drying process in such oils occurs through an oxidative free radical polymerisation reaction and results in the hardening of the paint film [1]. The drying of oils in paint films is important as it influences the properties and methods of application by the artist. Drying is also important in the restriction of undesirable pigment interactions. The black pigment copper sulphide is, for example, known to be produced on the interaction of copper ions with sulphide pigments such as cadmium yellow (CdS) [2]. Indeed in our own work we have been characterising the products of interaction of cadmium yellow and malachite using scanning electron microscopy and crystallography where copper sulphides have been observed to be produced by the interaction of these pigments in both aqueous and drying oil environments [3]. Although this problem has been observed to occur in dry paint films through the migration of copper ions [2], the complete drying of a paint film results in the immobilisation of a pigment and significantly retards the rate of reaction [3].

As drying the oils retards pigment interactions significantly, an understanding of the rate of drying is important in order to reduce the potential for reactions to occur in interacting paint layers. This is particularly important in restoration of valuable artworks where in order to maintain the character of an original painting, materials similar to those used by the original artist are used. In order to gain an understanding of the drying process, in particular in the presence of the pigments incorporated into linseed oil films, thermal characterisation of the paint films has been carried out. Thermal analysis has been successfully applied to the characterisation of paint films through the characterisation of the effect of drying agent and proportion of drying agent on the shape of the curve [1], the effect of aging of paint films on the curve [4, 5] and in the identification of medium and pigment used in artworks [6]. This paper also investigates the use of thermal analysis for the characterisation of the oils and paints used in artworks and reports some of the preliminary result of a differential scanning calorimetric characterisation of cold pressed linseed oil based paints incorporating lead pigments.

## Experimental

The materials used in this study are all commercially available art supplies. The CPLO used was a cold pressed windmill linseed oil supplied by Sthebeningen (Holland) and the red lead ($Pb_3O_4$) and lead white ($2PbCO_3{\cdot}Pb(OH)_2$) were supplied by Kremer Pigments (NY, USA). All materials were used 'as received'.

Pigments were blended into the CPLO in approximately 40% by mass of pigment. The paints were then mixed and 3 to 6 mg was placed into an open aluminium pan and placed in a TA Instruments 2920 MDSC differential scanning calorimeter (DSC) using a similar open

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1388–6150/$20.00

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aluminium pan as the reference. The samples were then heated at a rate of 5 K $min^{-1}$ in a static air atmosphere from room temperature to 300°C. The temperature was limited to 300°C as it was found that heating to higher temperatures resulted in boiling of the oil yielding poor curves above 300°C. In order to characterise the rate of drying, heating curves at 1, 2.5, 5, 7.5, 10, 15 and 20 K $min^{-1}$ in a static air environment were also measured. Temperature calibration of the DSC was carried out using indium, tin, zinc and lead as the standards while heat flow calibration was carried out using indium as the standard.

## Results and discussion

DSC heating curves for cold pressed linseed oil (CPLO) and CPLO pigmented paint specimens are shown in Fig. 1. Oxidation is observed in each case as exothermic behaviour in the curve. Two general processes are observed as the temperature is increased and are attributed to, initially, oxidative polymerisation and, at higher temperatures, complex oxidative degradation [1]. The onset temperature of the initial oxidative polymerisation process for the pigmented oils is observed in the range 50 to 60°C, at approximately 54°C for the lead white and 58°C for the red lead paints. Although similar onset temperatures for both lead pigmented paints were measured, a significant difference in the energetics of the oxidative polymerisation was observed with the red lead paint producing a more exothermic reaction than the lead white paint. The onset temperature for the oxidative polymerisation of the CPLO is observed at approximately 166°C. This onset is at a significantly higher temperature than those observed for the pigmented paints indicating that the pigments are activating the oxidative polymerisation process. This observation correlates with much of the work carried out on pigmented drying oils in the literature where lead, as well as other metal, salts have been observed to increase the rate of drying in linseed as well as other drying oils [1, 4].

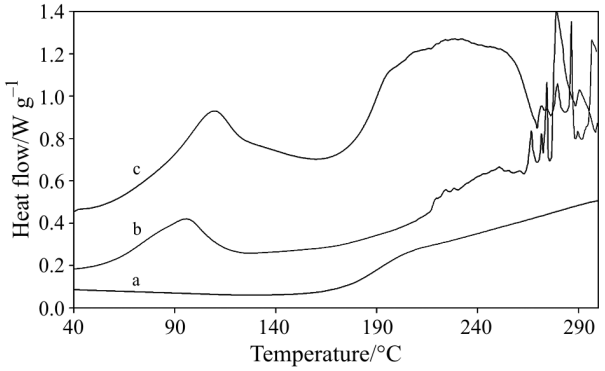


**Fig. 1** DSC heating curves for a – CPLO, b – CPLO and lead white and c – CPLO and red lead. Heating curves were recorded at a heating rate of 5 K $min^{-1}$ in a static air atmosphere

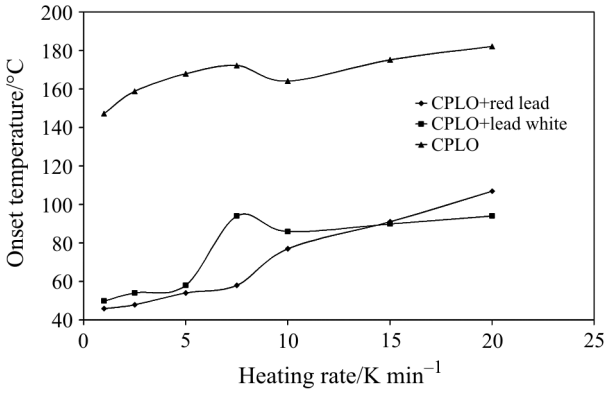


**Fig. 2** Plot of the onset temperature for oxidative polymerisation in CPLO and paints containing red lead and lead white pigments as a function of the heating rate

The process of the oxidation is observed to be through two steps; initially of oxidative polymerisation followed by oxidative degradation. In the experiments reported in this paper, the second process was surmised to be coupled with pyrolisation. All films recovered from the DSC were light to dark brown in colour. The dark nature of the residues is characteristic of pyrolisation and is the result of the inability of oxygen to diffuse into the paint film at a high enough rate.

In addition to measurement of the onset temperatures of oxidation at a single heating rate, the onset of drying was also investigated by varying the heating rate. The onset temperatures were measured and plotted as a function of the heating rate in Fig. 2. A smooth shift in the onset temperature of the oxidation process to higher temperature is not observed. Indeed, in all cases the mechanism appears to change as the heating rate is increased. In all cases there is a discontinuity in the data around 7.5 K $min^{-1}$ indicating a change in the mechanism of oxidation with increasing heating rate. A change in the mechanism is not unexpected as, for oxidation to occur, oxygen diffusion through the surface into the bulk of the paint film must occur. As this is a slow process, a change in the heating rate is likely to transform the mechanism from predominantly oxidative polymerisation to a polymerisation process where the non-oxidative mechanisms begin to dominate. The fact that such a transformation in the mechanism is observed makes the data unsuitable for kinetic analysis.

## Conclusions

The addition of inorganic lead pigments to linseed oil was observed to significantly reduce the onset temperature of oxidative polymerisation of cold pressed lin-

seed oil. This correlates with anecdotal evidence based on artist's reports [7] as well as the literature on the thermal characterisation of the drying process. An analysis of the rate of oxidative polymerisation of the linseed oil was found not to be possible as a mechanism change was observed in the thermal data as the heating rate was increased making the data unsuitable for kinetic treatment. It is, however, likely that lower heating rate measurements (in the range 0.1 to 2 K $min^{-1}$) would produce significantly improved data for kinetic analysis as the likelihood of a change in mechanism is reduced. Such measurements will be the subject of future investigation.

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