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Effects of acetic acid vapour on the ageing of alkyd paint layers: Multi-analytical approach for the evaluation of the degradation processes

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ABSTRACT

Interactions with volatile organic compounds (VOCs) are one of the main issues within the field of the preventive conservation of artworks. VOCs deriving from wooden frames and museum furniture consist in several aldehydes, formic acid and a high abundance of acetic acid. The aim of this study was to evaluate the interactions between alkyd paints and acetic acid that take place during the curing process of the paint layers. A set of reference Winsor & Newton alkyd paint layers was exposed to acetic acid vapour for six months to model these interactions. In order to evaluate the main degradation pathways occurring during the artificial ageing, a multi-analytical approach based on chromatographic and spectroscopic techniques was used. The results describe the main degradation processes of the organic and inorganic components used in the production of the alkyd resin paint.

1. Introduction

Alkyds paints are oil-modified polyesters synthesized from polyols, aromatic polybasic acids and different weight percentages of oil (or a source of fatty acids). They have been commonly used as commercial binders for paints and coatings since 1940 [1].

Alkyd paints are often modified with additives in industrial production to improve the physical proprieties of the resins and reduce the production costs. Possible modifiers are fatty acids, acrylic, styrene and silicone compounds, inorganic fillers and driers, and dispersing agents [1,2].

Preventing damage related to volatile organic acids and inorganic air pollutants is one of the main issues in the preventive conservation of artworks. The main sources of organic pollutants inside museums include wooden objects and wooden showcases, and interactions with the released volatile organic compounds (VOCs) can be potentially dangerous for the conservation of the paint layers in general, and alkyd paints in particular [3]. VOCs derived from wood are characterized by the presence of different aldehydes, formic acid and relatively high concentrations of acetic acid, which is the main pollutant released during the ageing of wooden materials [4]. The impact of these VOCs on natural varnishes used in restoration has been described in[5].

The aim of this study was to evaluate the interactions between alkyd paints layers and acetic acid during the curing cycle of the paint, in order to identify the main degradation pathways of the organic and inorganic materials used in the production of commercial paint.

A few ageing studies on alkyd resins have been described in the literature: infrared spectroscopy, thermal analysis and analytical pyrolysis coupled with gas chromatography/mass spectrometry are the current approaches used for the chemical characterization and the study of the curing of these polymers [6–10]. However, as far as we know, no detailed studies on the interactions between alkyd paints and acetic acid have yet been published.

In this study the ageing behaviour of a set of reference Winsor & Newton alkyd paint layers exposed to acetic vapour for six months were investigated using a multi-analytical approach based on integrated mass spectrometry [11], High Pressure Liquid Chromatography–Diode Array Detector, and Attenuated Total Reflectance Infrared Spectroscopy. In detail:

- Attenuated Total Reflectance Infrared Spectroscopy (ATR-FTIR) was used to investigate the chemical modifications undergone

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by the inorganic additives in the resin formulation during the artificial ageing of the reference layers.

- Gas Chromatography/Mass Spectrometry (GC/MS) analysis was used to obtain quantitative and qualitative information on the fatty acid content and on the presence of oxidation products in the lipid material [12–15].
- High Performance Liquid Chromatography–Quadrupole-Time of Flight (HPLC–ESI–Q-ToF) and Flow Injection Analysis (FIA–ESI–Q-ToF) were used to determine the triglyceride (TAGs) profile of the lipid fraction of alkyd paints [13,14].
- High Performance Liquid Chromatography–Diode Array Detector (HPLC–DAD) enabled us to obtain quantitative information on the phthalic acid content in the soluble fraction of the resin.

The combination of the five analytical techniques enabled us to fully characterize the main chemical modifications in the alkyd paint reference layers during artificial ageing in an acetic acid environment. Our results highlighted the effects of exposure to acetic acid vapour.

2. Material and methods

2.1. Alkyd paint samples

The reference layers were prepared on glass slides with 10 commercial artistic paint tubes from the Winsor & Newton “Griffin Fast Drying Oil Colour” series containing, according to the supplier, Winsor Red (PR170, PR188), Cadmium Red Medium (PR108), Winsor Lemon (PY3), Cadmium Yellow Light (PY35), Titanium White (PW6), Ivory Black (PBk9), Phthalo Green (PG7), Viridian (PG18), Phthalo Blue (PB15), and French Ultramarine (PB29).

During the first months of curing, the composition of the paint layers is variable due to the different oxidation speed rates, related to the catalytic effects of the pigment and dyes [8,16]. Thus, the reference layers were aged for nine months in indoor conditions prior to artificial ageing.

The 10 reference layers were then transferred into a glass vessel (11 L) containing 30 mL of 0.5% v/v of acetic acid solution, saturated with NaCl, giving an RH = 75%.

The vessel was conditioned for 24 h prior to the ageing experiment and was maintained at room temperature (average temp. 25 °C) during the ageing process.

Samples were collected after 1, 2, 3, 4 and 6 months of ageing in acetic acid rich environment, and the acetic acid and NaCl solutions were replaced after each sampling.

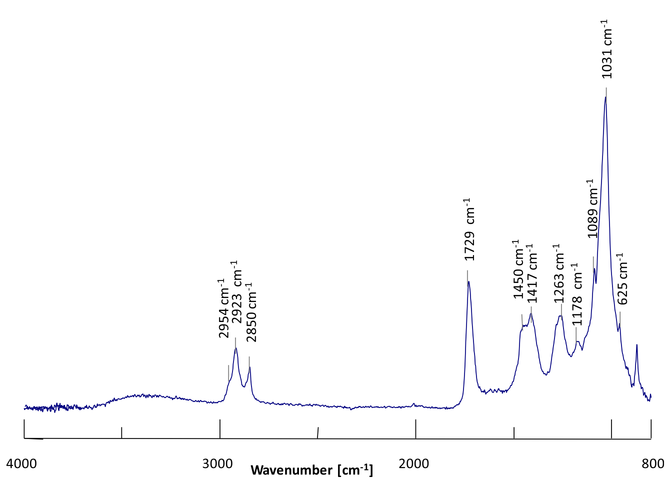

Fig. 1. ATR-FTIR spectrum of the Winsor & Newton “Griffin Fast Drying Oil Colour” containing ivory black as pigment (PBk9) after 9 months of natural ageing.

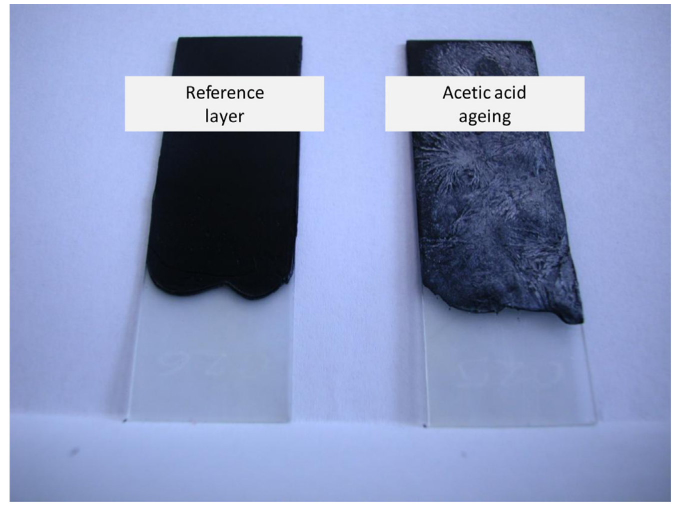

Fig. 2. Winsor & Newton “Griffin Fast Drying Oil Colour” (PBk9) reference layers: on the left, after 9 months of natural ageing; on the right, after 9 months of natural ageing plus 1 month of acetic acid exposure.

2.2. Materials and reagents

The solvents used for the GC/MS analysis were: diethyl ether, *n*-hexane and *iso*-octane (HPLC/MS grade; Sigma–Aldrich, U.S.A.). *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane used for fatty acid derivatisation was purchased from Sigma–Aldrich (U.S.A.).

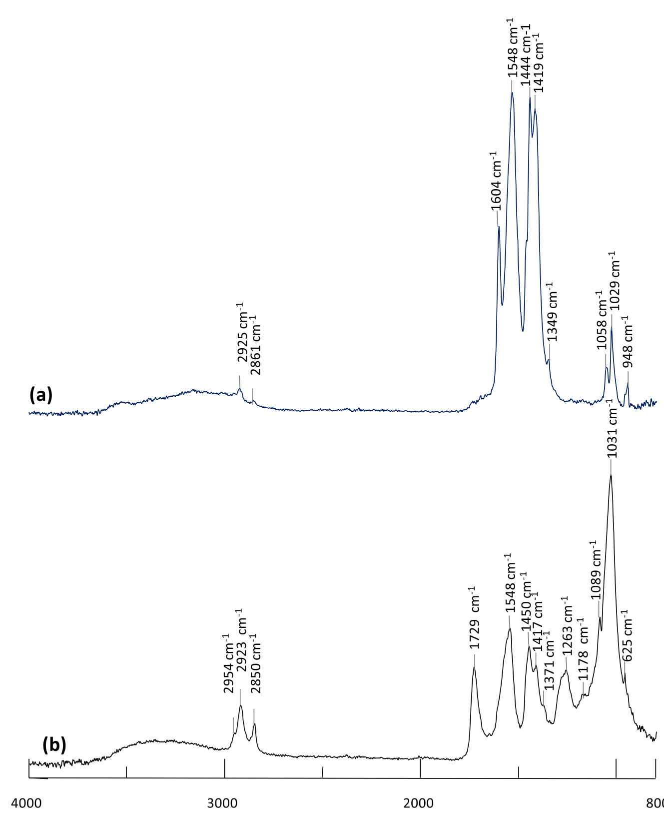

Fig. 3. ATR-FTIR spectra of the Winsor & Newton “Griffin Fast Drying Oil Colour” (PBk9): a) spectrum of the white layer formed on the surface of the paint layer; b) spectrum of the paint layer after removal of the white patina.