



Correlating thermophysical properties with the molecular composition of 19th century chrome yellow oil paints



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ARTICLE INFO

Article history:

Received 16 November 2016

Received in revised form

20 January 2017

Accepted 20 February 2017

Available online 6 March 2017

Keywords:

19th c. oil paints

Thermophysical properties

Chrome yellow

Fillers

Conservation

ABSTRACT

In the present study, we explore Dynamic Mechanical Thermal Analysis (DMTA) as a tool for assessing the physical performance in 19th century paints and to evaluate the parameters that influence the mechanical properties of the paint films. This data is particularly important for accurate life-time predictions as well as better conservation treatments. DMTA is used to study the thermophysical properties of chrome yellow (PbCrO₄) oil paints under the influence of common fillers found in 19th century chrome yellow oil paints: calcium carbonate (CaCO₃), barium sulphate (BaSO₄) and gypsum (CaSO₄·2H₂O). Oil paint mock-ups were dry to touch and included oil plus the single paint components (chrome yellow pigment and the three fillers) that were compared with 19th c. Winsor & Newton historic paint formulations. The fillers selected were applied with a ratio to pigment ranging from 10 to 40% in weight.

DMTA data revealed that the addition of solids (pigment and/or fillers) reduces the flexibility of the oil paint films, confirmed by the increase of the storage modulus (*E'*) and glass transition temperature (*T_g*). DMTA provided a clear differentiation between the thermo-mechanical behavior of the oil film and oil with inorganic compounds and, more importantly, pigment oil system versus oil with fillers. The data revealed that the pigment and filler system oil is modulated essentially by the presence of the filler irrespective of the individual filler behavior (as a single component) and its percentage (within the proportions used by Winsor & Newton in their 19th c. chrome yellow paints).

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1. Introduction

A 19th century drying oil, triglyceride based, can be transformed into an artist's paint by incorporation of a colourant (an organic or inorganic pigment), as well as other additives that can tailor the rheology and also influence the mechanical response of the dried paint film to internal and external stresses [1–7], Fig. 1 and Fig. 2A.

In the 19th century the major drying oils were based on polyunsaturated C₁₈ acids, oleic (C18:1), linoleic (C18:2) and linolenic acids (C18:3), and a small percentage of C₁₆ and C₁₈, palmitic

(C16:0) and stearic (C18:0) saturated fatty acids, Table 1 [5,8].

At that time, the most common fillers found in paint formulations were calcium carbonate (CaCO₃), barium sulphate (BaSO₄) and more occasionally calcium sulphate dihydrate (CaSO₄·2H₂O), commonly named gypsum [9,10].

1.1. Molecular characterization of artists' oil paints: drying process and molecular aging

Artists' oil paints are a complex organometallic matrix that has been subject of a systematic characterization in the recent decades [1–8], contributing with important and pioneering research to interpret both chemical and physical alterations of oil paints caused by the drying and ageing processes. The multidisciplinary team headed by Jaap Boon has made major contributions to our understanding of 15th-19th c. oil paint degradation phenomena and their impact on paintings [5,7,8,11–13]. At the same time, the concept of

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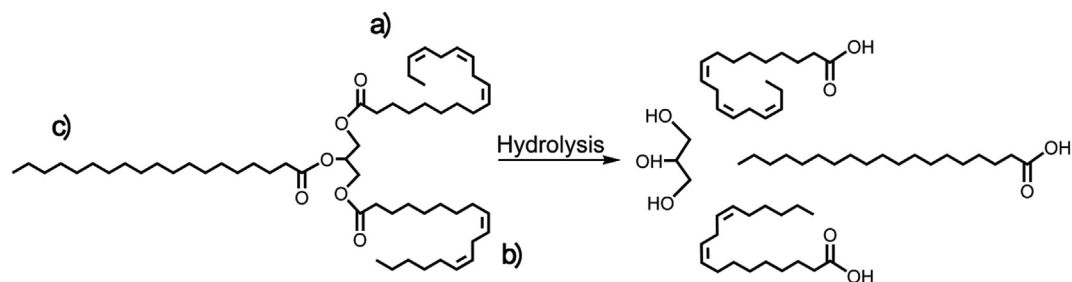


Fig. 1. General chemical structure of the triglyceride followed by its hydrolysis, in this example, into: a) linolenic acid; b) linoleic acid and c) stearic acid (2–8%).

Table 1

Fatty acid composition (%) of the main drying oils used in 19th century artists paints after van den Berg [5].

Oil	Oil (%)				
	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)
Linseed	4–10	2–8	10–24	12–19	48–60
Poppyseed	9–11	1–2	11–18	69–77	3–5
Walnut	3–8	0.5–3	9–30	57–76	2–16

historically accurate reconstructions was under development with the work of Leslie Carlyle [9,10,14–18], which provides reference material and insight into oil paint formulations as recently exemplified for 19th c. chrome yellow oil paint formulations developed by Winsor & Newton and the research carried out by Vanessa Otero et al. [19–21]. Within this framework, Raman and infrared spectroscopy proved to be powerful and complementary techniques for the characterization of the molecular transformations of naturally aged oil paints, offering a full identification of the metal carboxylates, an important component of an oil paint and its stability [8,22–24].

Based on the working model proposed by Jaap Boon [5,7,13], 19th c. artists' oil paint systems can be better described as a complex three-dimensional polyanionic network based on the glycerol ester with a crosslinked fraction of carboxylate anions stabilized by metal cations, Fig. 2 [5,7,13].

The drying process of the oil results from photooxidation and autoxidation reactions [25,26]. The reactivity of the double bonds of the unsaturated fatty acids promotes the formation of larger polymer chains through C–O–C or C–C bonds [8], Fig. 2B. C–O–C bonds may result from the reaction of oxygen and the double bond that leads to the formation of hydroperoxides [26].

In the curing and aging of an oil paint, at the same time that crosslinking takes place, hydrolysis of the ester functions to carboxylic acids occurs as well, Fig. 2B and C. Over time, hydroperoxides will transform into other reactive functional groups such as carbonyls that in turn will undergo Norrish type I and II photoreactions, and will lead to extensive chain scission and crosslinking [25–27]. As a result, in the paint system, the amount of glycerol, free fatty acids, diacids and crosslinking moieties will increase over ageing. Scission reactions will also promote loss of original material by formation of volatile fragments.

Taking into account the multiple and extensive degradation phenomena it is surprising that “a complete failure of the paint and loss of the picture” [12] is not observed more frequently. Boon has proposed that this is due to a self-repair mechanism based on the self-organization of carboxylates. In this model, the products of consecutive hydrolyses are stabilized by metal ions associated with the pigments or driers [7]. This structure is relatively stable due to the diacids formed by hydrolysis, and also because external

environmental factors can re-establish coordination with the metal carboxylate groups that remain attached to the network [7,28].

1.2. 19th century drying oils

Concerning 19th century oil processing methods, the so-called *drying oils* would undergo pre-treatment to achieve suitable qualities for artistic proposes. Besides being refined or clarified, the oil could be heated and metal ions as driers could be added to it enhancing the drying rate [29–32]; the presence of these transition metals promotes initiation reactions by favouring free radical formation and oxygen intake.

Litharge (PbO), was popular since historical times, and by the end of the 19th century other transition metals like zinc, manganese and later cobalt, were introduced in order to improve the drying capacity and to reduce toxicity issues [30]. Considering that the present work follows on the study of oil paintings from the second half of the 19th century, litharge was chosen as the drier for oil processing. The decision for this lead compound was supported by a previous investigation before a careful selection of historical recipes [17].

1.3. 19th century artists' paintings and paint layers

Paintings are a multi-layered system that includes not only the paint but also the first application over the canvas, known as ground layer, Fig. 3.

Non-absorbent grounds, oil grounds, start to be preferred on the 19th century as they were more flexible than the distempered ones (i.e. made with animal glue) [31]. Usually the ground layers were made with white powders such as lead white, chalk (natural calcium carbonate), gypsum and clay, and its absorption rate could be, among others, regulated by the amount of drying oil added into the mixture. As a common technique of this time, to build the pictorial composition a large number of paint layers would be laid over the ground.

As previously described, the study of the molecular ageing of oil paintings has enabled major advances in our understanding on degradation effects. However, the correlation between molecular characterization and the painting's mechanical and physical performance is still in its exploratory phase, especially concerning oil paintings. In this work, we will only focus on the oil paint layer to evaluate the potentiality of DMTA for its characterization over time.

1.4. Thermoanalytical studies

Physical and mechanical properties that have direct implications on paint performance can be defined by a variety of thermoanalytical techniques [33–39]. Important contributions were made by Odlyha et al. with the thermal analysis of paint films and primed canvas supports [34,35]. Any method that could allow and

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