



The drying of linseed oil investigated by Fourier transform infrared spectroscopy: Historical recipes and influence of lead compounds



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ABSTRACT

Lead compounds have been commonly used since the Renaissance period to increase the drying properties of oils. This article presents new insights on the mechanisms involved: Fourier transform infrared spectroscopy (FT-IR) has been used to investigate the effects of lead oxide on the drying process of linseed oil. The changes occurring during the drying of oil and the influence generated by the use of PbO were monitored by integrating absorption bands of interest such as the $\nu(\text{O}-\text{H})$ absorption band at 3500 cm^{-1} , and the $\nu(\text{C}-\text{H})$ in *cis* $\text{C}=\text{C}-\text{H}$ band at 3010 cm^{-1} . Results indicate that the addition of lead oxide accelerates the drying process and reduces the induction time (4 times with 5% PbO), without causing major changes in the mechanisms involved. An optimal amount of 5% PbO was determined, as compared to 1 and 20%. Historical recipes have been reviewed and the effect of specific oil preparation parameters such as the heating of oil while adding PbO addition and the addition of water has been investigated.

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1. Introduction

Oils used in historical paintings are natural drying oils, such as linseed, walnut or poppy seed oils. Their main components are triglycerides, which are esters of a mixture of saturated and polyunsaturated fatty acids responsible for air-drying properties [1]. The drying of linseed oil is a chemical process taking place spontaneously when exposed to the air, generally considered to be due to a process of autoxidation followed by polymerisation [1–8]. It is a multi-step reaction, starting with the autoxidation of $\text{C}=\text{C}$ bonds of the fatty acids chain into peroxidic compounds via an allyl stabilised radical. After an induction period attributed to the presence of natural antioxidants [2], the oil absorbs large amounts of oxygen. In the meantime, non-conjugated double bonds are converted into conjugated double bonds [5]. The reversible O_2 addition facilitates isomerisation of the unconjugated *cis*–*cis* bonds to successively more thermodynamically favourable conjugated *cis*–*trans* and *trans*–*trans* peroxy radicals [1,4]. The following cleavage of unstable peroxides and hydroperoxides lead to the formation of radical species, and to their recombination and/or to

their fragmentation into smaller alcohols and aldehydes [3]. In the sequence, the hydroperoxides undergo a polymerisation process following initiation, propagation and termination reactions [7–9]. This autoxidative crosslinking process is responsible for the formation of a solid film observed over time. The molecular weight grows mostly during the polymerisation step where $\text{C}-\text{C}$, $\text{C}-\text{O}-\text{C}$ and $\text{C}-\text{O}-\text{O}-\text{C}$ bonds are formed through the direct reaction between free radicals issued from the hydroperoxide decomposition [7]. The propagation of the polymerisation can also proceed through a hydrogen abstraction mechanism producing allylic radicals, or by addition of the ROO^\bullet radical to conjugated double bonds. After the addition reaction, the radicals allow polymerisation to follow, leading to epoxy and peroxide moieties. Although a film of linseed oil is touch-dry in a few days, the drying reactions continue for many years and, as cross-linking proceeds, a progressive hardening occurs, moderated by the presence of unchanged glycerides [2,10].

To fasten the curing process, the use of metallic driers appeared to have yielded successful results, for which it became a common practice among painters that remains up to date. By definition, “a drier for paint (...) will induce or speed up the setting or drying or solidification of a liquid oil film” [11]. Nowadays driers are typically metal soaps of either alkaline-earth metals or heavy metals [9,12]. Unlike most catalysts, driers can catalyse more than one chemical reaction in the autoxidative process. Driers can increase the O_2 uptake, reduce the induction time, and promote peroxide decomposition [11,13]. Different classifications of driers exist in the

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paint industry [9,14]. The historical one was based on their function namely (i) surface drier, (ii) through drier and (iii) auxiliary drier [9,15]. “Surface driers” are based on multivalent metals and as a consequence can undergo facile and reversible changes in oxidation states, which can promote the autoxidative curing process. They are also known to dry from the top down. “Through driers” promote curing beneath the surface of the coating. “Auxiliary driers” inhibit phase separation of the surface from the polymeric phase. Both cobalt and manganese-based driers can easily dry the surface of a produced film but leave the subsurface soft. Lead-based driers have the beneficial effect of more uniform drying throughout the entire film thickness, thus leading to films that have a good balance of hardness, toughness, flexibility and chemical resistance [9]. Another classification, that is most common nowadays, divides driers in two categories: those that affect the oxidation of oils, (which can be surface driers or through driers); and those that affect the polymerisation process itself, called secondary or sometimes auxiliary driers and which are often compounds containing metals with only one possible oxidation state (zinc, calcium, potassium, lithium, sodium compounds) [7,8,12]. Lead compounds can be considered as both oxidising driers and as polymerisation-affecting driers [13].

Litharge (PbO) is historically the most commonly used lead compound [16,17]. When litharge is mixed to oil, it provokes the saponification of some triglycerides and the formation of lead soaps [18]. At the end of the 19th century the paint industry started introducing soluble metal soaps directly (manganese and lead linoleates and resinates), instead of generating them in situ [17]. At the beginning of the 20th century, the efficiency of cobalt soaps made them very popular. Due to toxicological and environmental concerns, lead driers were phased out in the mid to late 20th century and were replaced by other through driers such as cobalt or zirconium-based ones [7,13,19].

In the context of an important industrial impact, the siccativ action of cobalt-based driers has been widely studied. Mallégol et al. [14] have shown that oxidative polymerisation mechanism of drying oils, with or without surface drier, is the same. They investigated the drying of films in the presence of cobalt drier, revealing changes in kinetics but not in stoichiometry of reactions. These changes can be explained by peroxide decomposition induced by cobalt. Conversely, while they have probably been the first and most used driers since the Antiquity, the drying actions and properties of lead-based compounds have not been investigated as thoroughly as modern (20th Century) driers. Tumosa and Mecklenburg [13] recalls that painters have used lead for a long time to improve their oil properties, but its action has not always been recognised by all chemists: in 1941, Bennett commented on the effect of lead driers: ‘By itself lead is not a powerful drying accelerator, at least for simple oil systems, and it does not appreciably alter the course of oxidation of the oil’.

In the present work, we have been investigating numerous historical recipes, in order to identify the most standard oil preparation method, which we used to prepare mock-up samples. As detailed below, lead can be introduced in oil under different forms, with different additional ingredients and under different temperature conditions. Among these recipes, mixing and heating oil with litharge was found to be the most common process. The short term effects of various lead compounds (in particular litharge) on oil in the synthesis of lead media (in cosmetics and paintings) have been previously studied by means of FTIR study [18,20]. In particular, the saponification process induced by lead compounds on oil triglycerides was monitored over a few hours. In the present paper, we aim to understand the way lead oxide added to linseed oil acts on the drying process. We follow the evolution during eight months of the FTIR spectra of PbO/oil mixtures, prepared in various conditions. The influence of PbO concentration and of the oil preparation method is investigated by means of ATR-FTIR. As a comparison,

PbCO₃ was also tested as a drier, at one specific concentration. To fully interpret our results, an extensive survey of the existing literature on the drying of linseed oil and its FTIR bands assignments has been done and presented.

2. Experimental

2.1. Historical sources and reconstitutions

We can see from historical sources from the 12th Century until now that the methods of refining and processing oils have not changed dramatically over centuries. One of the first recipes, from Eraclius (12th Century), advises to prepare the oil “for tempering colours” by boiling oil with lime, then adding ceruse and placing the mixture in the sun [21]. The addition of a lead compound in the preparation of drying oils has been commonly used since then. The main driers at the end of the Renaissance period are litharge, lead white, red lead (minium (Pb₃O₄)) and sulfate of zinc (ZnSO₄). Litharge was available in two varieties: silver and gold. The so-called silver litharge (yellow colour) was heated at higher temperature and reported to be a harder material than the gold litharge with a red colour [17]. The silver one was recommended over the gold one because it was more highly oxidised and would therefore make a more effective drier [17]. Lead white is composed of different proportions of cerussite (PbCO₃) and hydrocerussite (2PbCO₃, Pb(OH)₂) [22]; it is frequently referred as *ceruse* in the manuscripts.

We decided to focus our study particularly on the manuscript written by Turquet de Mayerne (1573–1654), an experimental Swiss chemist and friend of artists. This is an easily accessible manuscript compiling great knowledge about the preparation of colours, supports, oils for painting, gilding, ink [23]. Among 170 folios, 36 describe oil treatment and media preparation, underlying here the importance of such process. Folios can describe several recipes, a total of 58 recipes for oils have been found with more or less detailed which could include a simple note about the preferred use of siccativ oil and/or the complete recipe of oil preparation process. Some recipes (folios 94 and 143) indicate one or several “washing steps” with water. For example, in folio 94, the oil is first filtered through sand and then added to water. The filtration or addition of sand would help the oil purification by removing plant mucilage. Further treatments aim to whiten the oil and/or making it more siccativ. To lighten the oil, it is usually recommended to place it in the sun. As a secondary effect, oil placed in direct sunlight with periodic stirring, thickens. That is why it is sometimes suggested to carry out the bleaching process at a time of the year when the sun is not too strong, as in March (folio 94, 93), to prevent a too strong thickening. On the contrary, other recipes advice to expose the oil to the sun during warm weather, as the thickening is associated to an increase of the oil siccativ. Another method of bodying the oil is to heat it. Various “ingredients” can be added during heating or simple bleaching process, mainly siccativ materials. The most common are the lead compounds and the 29 recipes mentioning the use of lead compounds in the Turquet de Mayerne manuscript are listed in Table 1. *Litharge* is the most cited (25 recipes), with *lead white* present in 11 recipes and *ceruse* in one recipe. It is probable that *ceruse* designates here the white lead-based pigment without distinction of composition. The terms litharge or litharge of gold are almost equally used and we cannot state whether this distinction is made purposely or not. One recipe (folio 135) recommended that lead white should be mixed with oil, together with bread (“*made into crummes*”) and sawdust, placed in the sun for four or five days, stirring the ingredients together five or six times a day. Bread might be added to absorb the water from oil: 7 recipes mention it (4 with white bread and 3 with crust of bread) and sawdust would absorb any remaining plant mucilage and lecithin [24]. Four recipes

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