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The synergistic influence of metal cations on the drying and viscosity of linseed oil assessed by means of model samples containing synthesised metal carboxylates

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Abstract

The recent multi-analytical study carried out on the Van Eyck's *Ghent Altarpiece* showed the simultaneous presence of several kinds of metal carboxylates in oil-rich glaze layers. This outcome raised the question whether these carboxylates had already formed during the preparation of the oil binder by the artists. In the case of early-stage formation, they may have had an impact on the drying rate of the resulting oil, as well as on its handling properties. This hypothesis was investigated using a model system of in-house-prepared linseed oil containing incremental concentrations (2–5–10 wt.%) of relevant metal carboxylates (i.e. Ca-, Zn-, Cu-, and Pb oleates and stearates). This paper describes the influence of these type of molecules on the drying rate of linseed oil and, to an extent, on its viscosity. The drying time of the linseed oil, to which one or more metal carboxylates were added, was measured with a drying recorder while the viscosity was assessed with a rheometer. When introduced together, some of these metal carboxylates act in synergy to shorten the drying time with respect to the situation when the same metal carboxylates were added separately to linseed oil. Mixtures of Ca- and Zn-oleates proved to have a larger effect than other binary combinations. Addition of two metal oleates (combination of Ca/Zn/Cu/Pb) reduced the drying time even more. On the other hand, specific combinations of three metal stearates and/or oleates also demonstrated a significant synergistic effect towards increasing the viscosity of the binder. Especially combinations of Ca/Zn/Cu and Ca/Zn/Pb stearates and oleates gave rise to the highest level of linseed oil viscosity increase, when compared to the situation in which the same metal carboxylates were added separately.

Keywords Metal carboxylates, Metal soaps, Oleates, Stearates, Oil-containing binding media, Netherlandish painting, Fifteenth century

Introduction

The first two conservation phases of the *Adoration of the Mystic Lamb*, the masterpiece by Jan and Hubert van Eyck (ca. 1430–1433), also known as the *Ghent Altarpiece*, were dedicated to the exterior of the wings (closed configuration) and the lower register of the interior (open configuration) (Fig. 1), respectively. These campaigns offered a privileged opportunity to conduct an in-depth study of the techniques and materials used for the creation of such a masterpiece. Some practices employed by the Van Eyck brothers are similar to those that were

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Fig. 1 *The Adoration of the Mystic Lamb (Ghent Altarpiece)*, by Hubert and Jan van Eyck. Completed by 1432. Shown open, 375 × 514 cm. Upper register before restoration and lower register after restoration. (Cathedral of St Bavo, Ghent; ©KIKIRPA)

generally used by other fifteenth-century Netherlandish painters [1–3]. The wood panel was covered with preparatory layers (ground, underdrawing, and isolation), and the image was then built up with layers of opaque and transparent paints [1, 3, 5]. The van Eyck brothers employed and refined the technique of superimposing translucent thin layers, rich in oil medium, with low pigment content: hereafter referred to as glazes. This allowed them to create an extraordinary sense of depth and relief, as well as deep colours [1–5]. To achieve these optical effects in the *Ghent Altarpiece*, it is clear that a high-quality oil binder was employed, which dried well, was easily spreadable, and at the same time ensured the painting was durable [4, 5]. Unravelling the composition and formulation of this binder has occupied many writers, artists and scientists, since the fifteenth century, leading to a variety of hypotheses [4]. The recent investigation conducted during the treatment of the *Ghent Altarpiece* [5] raised some new questions that were further explored in this research.

During the two first conservation and research campaigns conducted on the *Ghent Altarpiece*, Macroscopic X-ray fluorescence (MA-XRF) scans showed the simultaneous presence of Pb, Zn, Ca, and Cu-containing compounds in red and/or brown glazes [5, 6]. In parallel, the chemical analysis of numerous samples taken in associated areas revealed the significant presence of metal carboxylates in the paint layers rich in oil medium [5, 6]. The exact type of carboxylate was

not pinpointed for all samples, but their presence was inferred from the incidence of metal ions in carboxylate-rich areas. Zinc was detected either in the form of zinc sulphate by means of Synchrotron X-ray Absorption Near Edge Structure (SR-XANES) or in the form of zinc carboxylates by ATR-FTIR [5]. Calcium-containing compounds are generally present, not only as calcium carbonate (calcite) in the ground layers and in many glazes, but also in the form of calcium phosphate (hydroxyapatite). This compound was identified with Micro Raman Spectroscopy (MRS) and Synchrotron radiation X-ray powder diffraction (SR-XRPD), mainly in the priming layer on the exterior of the wings [5]. Lead and copper compounds are abundantly present in the glazes, such as lead white (hydrocerussite) and verdigris (copper acetate); very often their diffuse presence was observed in carboxylates-rich samples [5]. In some red areas, the chemical analyses conducted with High Performance Liquid Chromatography (HPLC) identified kermes lake as a main component (sometimes applied on top of a vermilion-containing underlayer). In the brown glazes, the main pigments identified were coal, charcoal, and bistre from soot combined with small amounts of brown earths [5]. The lakes, coal, and bistre pigments are known to be poor driers, and thus needed to be associated with drying agents. Additives such as zinc sulphate and calcined bones, as well as fast-drying pigments such as verdigris and lead white were often identified in the red and brown areas [5].

Based on the analytical results [5], it is suggested that some of the metal carboxylates detected in the oil-rich glazes were metal soaps formed during the preparation of the binder. This possible formation of metal soaps would have been promoted by the introduction of additives and/or pigments along with the heating of linseed oil, as it is often recommended in historical recipes [7–10]. If the metal soaps were formed at this early stage of the painting process, they could have had an impact on the properties of the oil medium [11–17]. Indeed, as described in modern literature, metal soaps, depending on the type of metal compound and the type of acid, may act as driers, being catalysers—or co-catalysers—of the chemical reactions involved in the autoxidation and polymerisation processes of linseed oil [11–19]. Furthermore, some metal soaps may also have an influence on the handling properties of the paint—acting, for instance, as thickeners, wetting agents, dispersive agents, etc. [11–13, 17].

Among the metal-containing compounds identified in the oil-rich layers of the *Ghent Altarpiece*, the evidence of zinc sulphate fits well with the hypothesis that *white copperas* (zinc sulphate) [10, 20] was used as one of the driers of the oil binder. Such a hypothesis was already proposed by Eastlake in the nineteenth century, on the basis of his study of medieval treatises, [9, 10, 21, 22] and further supported by Spring's study of several Van Eyck paintings [23, 24]. Furthermore, the detection of calcined bones in several paint samples from the *Ghent Altarpiece* is reminiscent of the fifteenth century *Strasbourg manuscript*, where calcined bones and zinc sulphate are mentioned as ingredients in a recipe for the preparation of the so-called *Oleum preciosum* (see Supplementary information, S1) [10]. However, it was first highlighted by Keller, then by Kneepkens, that this document may be incomplete, as their reproduction of the historical recipe did not result in a clear and fast drying oil [20, 25].

The possible intentional mixing of metal driers in low quantities (i.e. white zinc vitriol and calcined white bones as mentioned in the recipe) with the oil seems to correlate with our analytical results on the *Ghent Altarpiece* [5]. It is not unthinkable that other pigments, from which metal soaps can form, were added during the modification of the oil binder, such as lead- or copper-containing pigments. In particular, lead-based compounds seem logical, as they were likely the most-used driers since antiquity, as suggested by their significant occurrence in historical recipes [7–9, 26]. Based on the analytical outcomes and the literature research in old and modern written sources, the authors suspect that such an oil medium was used for preparing the red and brown glazes, which would dry very slowly without modifications to the oil binder [5, 11, 19]; however, in order to assess any potential link between the composition of the

Van Eyck's glazes and the practice described in the recipe, one aspect needed to be clarified first. It remained unclear whether the metal carboxylates encountered in the samples of the *Ghent Altarpiece* were, at least in part due to the metal soaps that had already formed during the preparation of the paint medium, or whether they only occurred later during the natural aging of the painting. If formed before the application of the oil paint, the next question is if these metal soaps indeed enhance its drying rate and handling properties, and if the combination of more than two metal soaps influence these properties further.

Similar questions about the early-stage formation of metal soaps during the painting process were recently investigated [11, 17, 19, 27]. For instance, Cotte et al. demonstrated that the addition of lead compounds during the heating of linseed oil can lead to the formation of lead soaps, resulting in the shortening of the drying time and the modification of the rheological behaviour of the binder [19, 26, 28]. Other studies showed how zinc, calcium and copper ions are likely to form metal soaps naturally in the paint film [14, 16, 17, 29–34]; however, only few researches have focused on the effect of the simultaneous addition of calcium and zinc with other metal cations. The efficiency of several combinations of modern driers, such as metal ions bound to 2-ethyl hexanoic acid, used in the modern alkyd paint industry has already been reported [12, 13, 17, 34–36]. These focused on commercial driers, investigating associations of primary driers (also called active or oxidation driers, e.g. cobalt, manganese) with secondary (also called through driers, e.g. lead, copper) and auxiliary driers (e.g. calcium, zinc) [12, 13, 17, 19, 35, 36].]. For instance, Dubrulle et al. [13], found synergistic effects with combinations of Co/Zn, Mn/Zn, and Fe/Ca on the drying of fatty acid methyl esters, while Mallégo et al. [35] demonstrated the benefit of using the combination of Co/Ca to obtain a more uniform drying of the alkyd coatings. Their studies illustrated how secondary and auxiliary driers, in combination with primary driers, can act as co-catalysers and promote a more uniform and complete curing of the coating [12, 13, 17, 19, 25]. However, none of these researches investigated associations of secondary driers with auxiliary driers in the context of traditional oil painting, as it is the case in the present paper. Considering the limited comparability of modern driers used in the paint industry with the metal carboxylates encountered in traditional oil painting, different mechanisms are expected.

Although lacking any explicit understanding of the chemical pathways that give rise to metal soaps formation, it appears that painters in the fifteenth century had an empirical knowledge of the benefits associated with introducing small amounts of specific substances in oil

[19, 27, 37]. As reported in the publication of Sanyova et al., metal cations were often present in small amount in the paint samples of the *Ghent Altarpiece* [5]. Zinc, in particular, was sometimes hardly detected in the paint micro-samples using SEM–EDX, although the corresponding sampled area of the *Ghent Altarpiece* scanned with MA-XRF shows its quite strong evidence [5]. The authors suggest that the Van Eyck brothers had mastered the skill to combine the additives to boost their influence on the drying time and handling properties of the binder, while minimizing the risk of causing detrimental effects that are often associated with an excess of driers (protrusions, loss of gloss, cracks, wrinkling, etc.) [5, 14, 16, 17]. The main purpose of the current investigation is to examine this hypothesis by assessing the impact of the controlled and accurate addition of various synthesised metal carboxylates on the properties of the oil-based medium.

Assessing the influence of several metal carboxylates on the drying time of linseed oil appeared to be of primary significance for this research, as obtaining an oil medium that dries quickly is essential to allow the superimposition of oil-rich glazes, characteristic of the technique used by the Van Eyck brothers [1–5]. As a complementary study, their influence on the oil viscosity was assessed as well, in order to substantiate the results. Viscosity characterises the resistance of a fluid to flow, and is defined as the ratio between the shear stress and the shear rate [37–41]. It is an important property to consider when studying painting technique, as the viscosity of oil paints should ideally be adaptable by the artist according to the desired effect. For the application of thin smooth glazes across large surfaces, viscosities between 100 and 500 mPa·s at low shear rate are often preferable to avoid sagging; however, the viscosity must not be too high either, so that the oil paint will remain easily spreadable and achieve good levelling [20, 37, 41]. As the amount of pigment is very low in the glazes, it is assumed that the viscosity of the layers is mainly related to the behaviour of the oil medium [37, 38]. Based on this assumption, this research is focused on the influence of various metal carboxylates on linseed oil without addition of pigments, in order to assess if they could play a role in the formulation of the glazes.

By characterising oil samples containing synthesised metal carboxylates with a drying recorder and a rheometer, this approach allowed us to assess the impact of these molecules on the drying rate and the viscosity of the binder in a quantitative manner. This well-defined system of experimentation was used to compare several metal carboxylates to evaluate their influence on the drying time and the viscosity of the resulting oil medium and to highlight potential synergistic effects when the metal carboxylates are added in combination. However, it must

be pointed out that these experimentations investigating a select few synthesised metal carboxylates only offers a limited comparison with traditional oil paintings, where several kinds of metal carboxylate complexes may form in situ [14, 16, 17, 28, 32]. Future research to investigate the impact of metal carboxylates formed naturally during the preparation of the paint and/or oil medium is foreseen to complement this preliminary investigation.

Methods

Synthesis of metal carboxylates

Metal carboxylates were synthesised by a precipitation process involving metal salts and fatty acids, following procedures that are described in detail in other publications [17, 42–44]. Materials were of analytical grade and obtained from Sigma-Aldrich®. Based on the results of the recent analyses carried out on the *Ghent Altarpiece* [5, 6], zinc, calcium, lead, and copper were selected as metal cations, respectively used in the form of zinc sulphate, calcium hydroxide, lead nitrate, and copper sulphate. The fatty acids chosen for the synthesis of metal carboxylates were saturated stearic acid (C18:0) (purity grade ~99%) and unsaturated oleic acid (C18:1), both present in linseed oil. Each metal carboxylate was obtained by dropwise adding a sodium hydroxide solution (0.5 M) to an alcoholic solution (ethanol) of carboxylic acid (0.2 M) at 70 °C, with continuous stirring for 15 min. An aqueous-alcoholic solution (water/ethanol 1:1) of a metal salt (0.4 M) was then added in the same way, at 70 °C, with continuous stirring for 30 to 45 min. The resulting precipitate was then filtered and washed with warm water and ethanol, and allowed to dry for several hours.

Preparation of the oil samples with synthesised metal carboxylates

Once produced, the metal carboxylates were added to raw linseed oil, freshly extracted from a single batch of linseeds of the cultivar ‘Nathalie’, that is produced organically by Van de Bilt Zaden en Vlas® for the flax industry [45]. Cold extraction of the oil was conducted in-house with a small stainless-steel press originally manufactured for the food industry (CGoldenwall®), at room temperature of 25 °C. Commercial linseed oil was not used to avoid any unknown pretreatments that might affect the binder properties.

In the oil prepared in this manner, up to four different synthesised metal carboxylates were dispersed at different mass percentage levels (1, 2, 3.5, 5, 7, and 10 wt.%). The concentrations of metal carboxylates were defined by weighting (balance with 5 decimals). The choice was made to prepare the oil samples at fixed mass concentration; however, it is relevant to consider the molar

concentration of each metal carboxylate as well, in order to correctly interpret the results. The molar concentration of each metal carboxylate is reported in Table 1 and will be further discussed in the ‘Results and discussion’ section.

To produce the modified oil samples, the metal carboxylates were ground in the raw linseed oil with a mortar for 5 min. Each oil preparation mixture was then heated with continuous stirring for 30 min at 70 °C, in order to ensure the dispersion of the metal carboxylates in linseed oil. For combinations of two, three, or four metal carboxylates, an equal amount of each single metal carboxylate was weighted separately and then ground together before being added to the linseed oil. For instance, for a mixture prepared with two metal carboxylates to reach a total concentration of 5 wt.%, each metal carboxylate was weighted at 2.5 wt.%. In total, approximately 200 oil formulations were produced in this manner.

Fourier transform infrared spectroscopy

The purity of the synthesised metal carboxylates was assessed by Fourier-transform infrared spectroscopy (FTIR Hyperion 3000, Bruker coupled to a

Mercury-Cadmium Telluride–MCT detector). The samples of metal carboxylates were mounted in a diamond compression cell and analysed by FTIR-MCT in transmission mode. Spectra were acquired in the 4000 to 450 cm^{-1} range, with 4 cm^{-1} spectral resolution and accumulation of 128 scans.

Drying measurements

A drying recorder BK10[®] purchased at Labomat[®] was used to measure the drying rate of each modified linseed oil. The measurements were conducted at room temperature with relative humidity between 40 and 50%. With this method, each oil sample is applied with a thickness of 50 μm on a glass strip (25 mm×310 mm), using a film applicator (25 mm wide), also obtained from Labomat[®]. A motor-driven needle travels along the strip, during a preset travel time (6, 12, 24, 48, or 72 h) (Fig. 2). The drying time in hours is then assessed with a graduation scale by measuring the mark left by the needle in the oil film (Fig. 3). This measurement of the mark is based on the ASTM D5895-03 and ISO 9117-4 standards that identify four different stages of drying time (Fig. 3) [46]: (1) *Dry to touch*: the needle creates a pear-shaped mark at the top of

Table 1 Table providing the molar concentration of each metal carboxylate in 5 g of linseed oil (mM)

Molar concentration (mM)									
Weight concentration (wt.%)	Mass (mg)	CaSt ₂	ZnSt ₂	PbSt ₂	CuSt ₂	CaOl ₂	ZnOl ₂	PbOl ₂	CuOl ₂
1	50	15	14	12	14	15	14	12	15
2	100	31	29	24	29	31	29	24	29
3.5	175	54	52	42	52	54	51	42	52
5	250	77	74	6	74	77	74	6	74
7	350	107	103	84	103	108	104	85	104
10	500	153	147	121	147	154	148	121	149

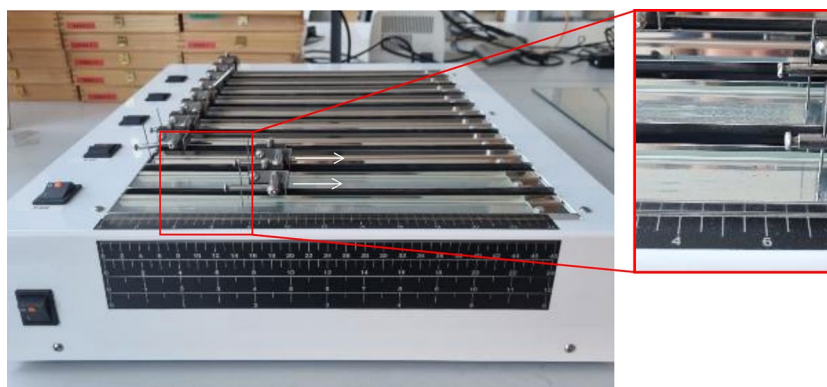


Fig. 2 Drying recorder BK10[®] in use. The needles travel along the glass strips where the oil sample was previously applied. The white arrows on the picture indicate the direction of the needle's movement

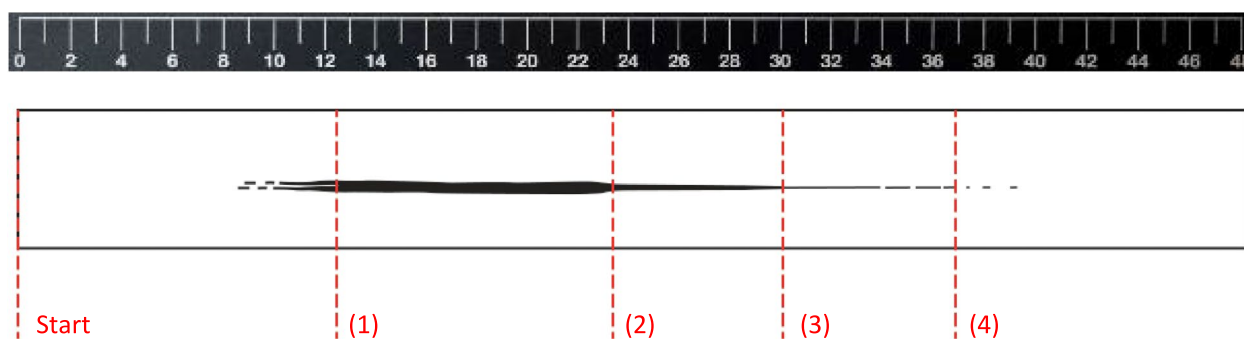


Fig. 3 Graduation scale (in hours) and scheme of interpretation, based on ASTM D5895-03 and ISO 9117-4 standards. The mark depicted in the scheme represent the mark that would be formed by the needle in the film during the drying time. (1) Dry to touch, (2) Non-sticky state, (3) Surface drying, (4) Final drying time

the film, this later becomes solid and dry to touch at the end of the phase. It is still a bit sticky under the finger. (2) *Non-sticky state*: the needle begins to leave a continuous sharp mark and the non-sticky state is achieved at the end of this phase. (3) *Surface drying*: the needle moves across the surface of the paint film and leaves a very thin track that is sometimes interrupted in small areas. (4) *Final drying time*: the needle no longer penetrates the film and gradually leaves no mark. The complete drying of the oil samples discussed in the results section corresponds to this final stage.

Each oil sample was measured twice to assess the reproducibility. The relative standard deviation for the mixtures studied varies between 4 and 6%.

Viscosity measurements

The viscosity measurements were carried out on a controlled shear rate rheometer/viscometer (Rheosys Merlin VR[®]) equipped with a plate spindle of 30 mm diameter (PP30), at a temperature of 25 °C and relative humidity between 40 and 50%. The Rheosys Merlin VR[®] measures the fluid parameters of shear stress and viscosity at given shear rates. In this investigation, each oil formulation was characterised at one speed (50 RPM), which allows to compare the viscosity of each oil sample at the

same shear rate (59 s^{-1}), even though this does not provide a complete overview of their rheological behaviour. This speed was selected as a good reproducibility was obtained for each sample at this shear rate. Oil samples were stored in closed bottle, away from the light. The viscosity measurements were conducted on each oil sample directly taken from the bottle, a few days after its preparation. Each measurement was repeated twice to assess the reproducibility.

Results and discussion

Visual observations

During the synthesis process, the rate at which a precipitate appeared was dependent on the types of metal ions and fatty acids. All metal stearates, as well as Ca and Zn oleates, generally precipitated in less than 5 min, while Cu and Pb oleates took up to 45 min. The resulting metal carboxylates presented a similar coloration to the one of their respective salts; copper produces a greenish colour, while zinc, calcium, and lead form whitish carboxylates (Fig. 4).

Once introduced in linseed oil (as described in the method section) the metal carboxylates may have an influence on the colour of the oil, especially in the case of copper-containing mixtures which became

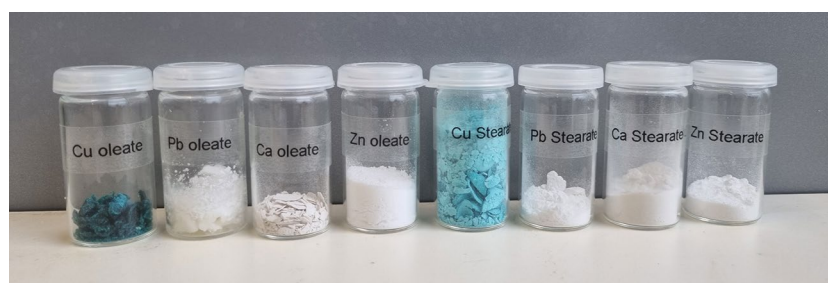


Fig. 4 Metal carboxylates obtained with the precipitation process. From left to right: Cu, Pb, Ca, and Zn-oleates, Cu, Pb, Ca, and Zn-stearates

greenish (Fig. 5). Oil samples prepared with oleate and stearate of zinc, lead, and calcium remained transparent and light. The colour properties of synthetic carboxylates are not necessarily the same to those found in paintings, as these properties depend on the way metal carboxylates are formed in situ [17, 30]. Nevertheless, in the case of copper-based compounds, which present a significant coloration, an impact on the final appearance of the glazes is expected. For this reason, it assumed that copper-based compounds would preferentially have been used in greenish and/or dark areas of the painting.



Fig. 5 From left to right: pure linseed oil, linseed oil with 5 wt.% of zinc oleate, with 5 wt.% of Pb oleate, with 5 wt.% of Ca oleate, and 5 wt.% of Cu oleate

Fourier transform infrared spectroscopy

The FTIR analyses confirmed that the precipitation process from metal salts and fatty acids produced oleates and stearates of zinc, calcium, lead and copper, in correlation with reference spectra found in literature [43, 44]. After precipitation, the infrared bands corresponding to C=O stretch of the fatty acids (around 1700 cm^{-1}) disappeared, being replaced by the characteristic bands attributed to COO^- symmetric and asymmetric stretch of each metal carboxylate between 1600 cm^{-1} and 1400 cm^{-1} [43, 44] (Fig. 6).

Drying measurements

Measurements conducted with the drying recorder indicated that the in-house-produced raw linseed oil dries in about 120 h. Considering that the drying state described with this method is not the complete curing of the oil, but the final solidification of the surface. This value was taken as a reference to assess the influence of metal carboxylates on the drying time of linseed oil. The systematic measurements of oil samples illustrated that, in general, metal oleates reduce the drying time of linseed oil more efficiently than metal stearates. For instance, an oil sample containing 10 wt.% of lead oleate featured a drying time of less than 30 h, while the drying time of an oil sample containing 10 wt.% of lead stearate was measured to be more than 72 h.

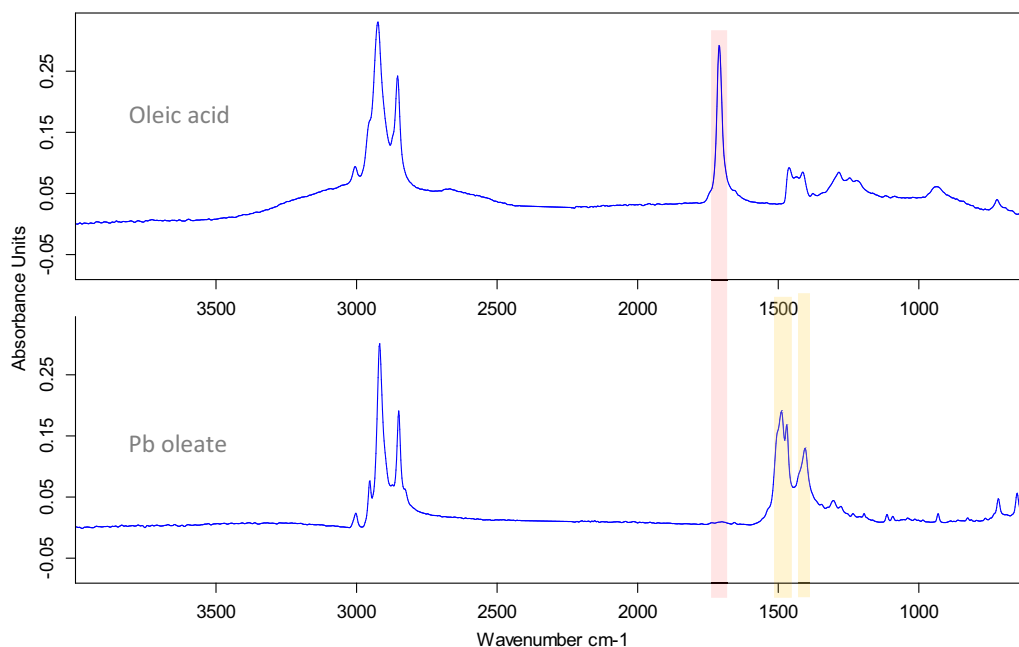


Fig. 6 Top: FTIR spectra of oleic acid. Bottom: FTIR Spectrum of lead oleate produced by precipitation process. The C=O stretch of the fatty acid (1710 cm^{-1}) disappeared (highlighted in red) and characteristic bands of lead oleate appeared ($\nu_{\text{as}}(\text{COO}^-)$: 1504 and 1487 cm^{-1} ; $\nu_{\text{s}}(\text{COO}^-)$: 1403 cm^{-1}) (highlighted in yellow)

As highlighted in other publications [14, 16–18, 28, 29, 32–34], the effects of the metal carboxylates strongly depend on their structure and solubility in linseed oil. It was reported that the solubility of metal stearates in liquid linseed oil at room temperature is very low, which may cause the irreversible crystallisation of the metal soaps in oil paint [14, 18, 28, 32]. On the other side, metals bound to the unsaturated oleic acid are expected to present a higher solubility, resulting from a more disordered structure of these molecules in the oil at room temperature [16, 17, 34]. As a consequence, the metal ions are expected to be more available for reaction in metal oleate complexes than in metal stearate complexes. This may be the reason why the metal oleates investigated in this study have a more significant impact on the drying time of linseed oil than the metal stearates; however, further investigations are needed to characterise the exact structure of the metal carboxylates in the model samples in order to validate these hypotheses.

As most of the oil samples containing metal stearates indicated a drying time above 72 h, only the results obtained for oil samples containing metal oleates will be shown and further discussed in this section dedicated to the drying measurements (Fig. 7).

One metal carboxylate in linseed oil

As shown in Fig. 7, these results indicate that among the single metal oleates added to linseed oil, lead oleate is the most efficient in reducing the drying time (between 28 and 45 h depending on the mass concentration), followed by copper oleate (between 38 and 43 h), while zinc oleate

induce only a minor reduction of the drying time respect to linseed oil alone (between 106 and 118 h).

As these oil samples were prepared according to fixed mass concentrations of metal carboxylates, it must be pointed out that the molar concentration of Pb oleate in these mixtures is lower than the molar concentration of the other oleates tested (at 10%, the molar concentration of each metal oleate added separately in linseed oil is 0.121 M of Pb, 0.148 M of Zn, 0.149 M of Cu, and 0.154 M of Ca). This means that, at same molar concentration, lead oleate could possibly reduce the drying time of linseed oil even more significantly in comparison to Zn-, Cu-, and Ca-oleates.

Combinations of two metal carboxylates in linseed oil

The measurements summarised in Fig. 8 illustrate that combinations of calcium oleate and zinc oleate at 5 and 10 wt.%, accelerate the drying time of linseed oil further, in comparison to situations where these metal oleates were added separately to the oil.

When added by themselves, the measurements indicate that zinc and calcium oleates are significantly less efficient dryers in comparison with lead and copper oleates (Fig. 7). But, at 10% of mass percentage, the combination of calcium oleate and zinc oleate (0.077 M of Ca and 0.074 M of Zn) allows to reach almost the same drying time as when only lead oleate (0.121 M) is added to the oil at equal mass concentration (31 h for the Ca/Zn combination; 28 h for Pb). Considering the lower molar concentration of Pb oleate in comparison to the molar concentration of Ca and Zn oleates added together

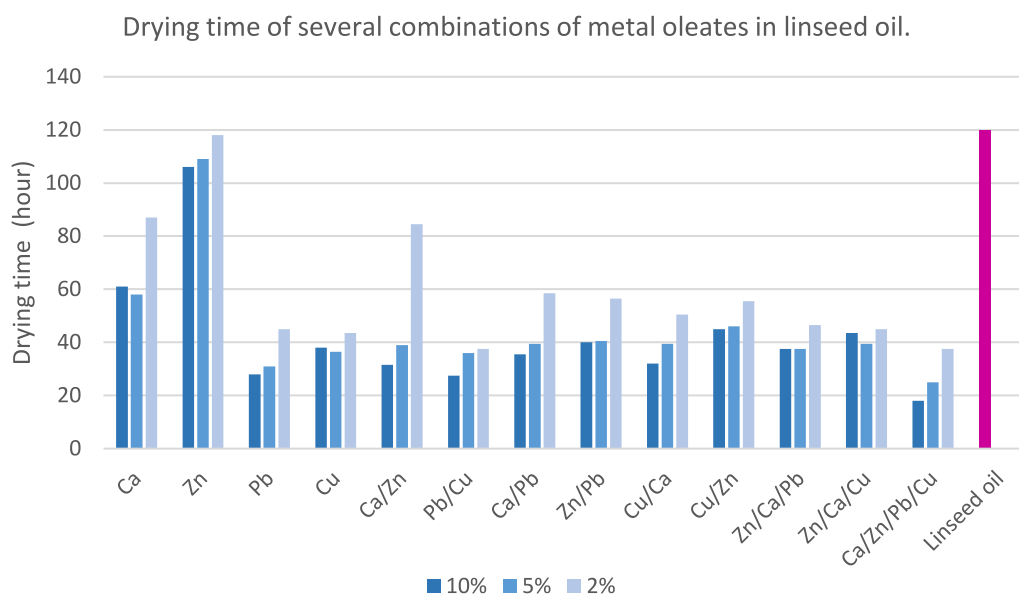


Fig. 7 Drying time of linseed oil containing different combinations of metal oleates, added in several mass percentages (2, 5, and 10 wt.%)

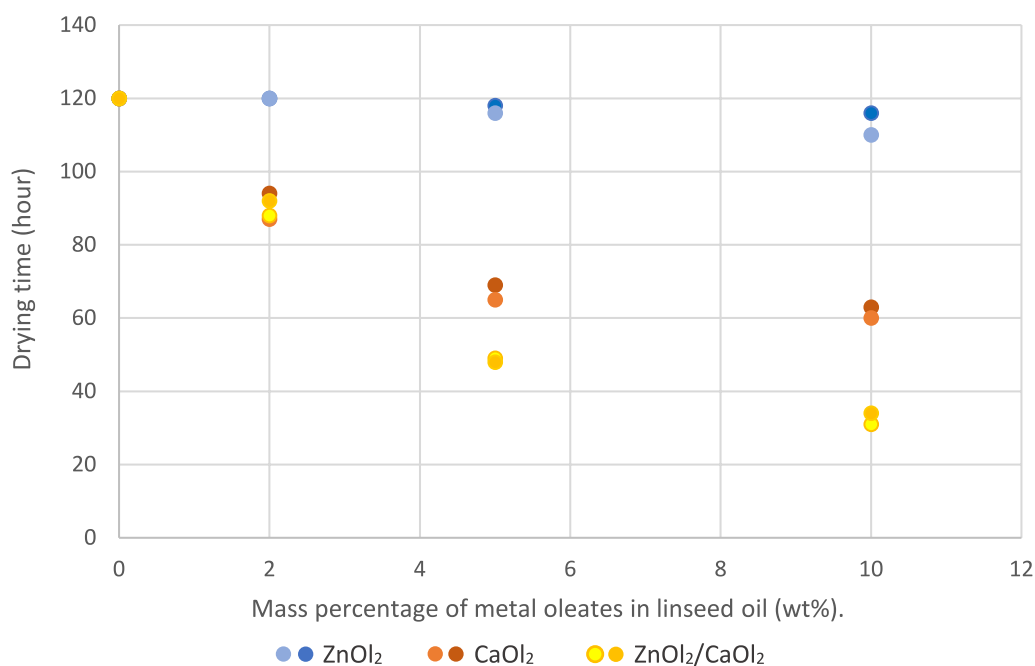


Fig. 8 Evolution of the drying time (hour) of linseed oil with increasing concentration of zinc oleate (ZnOl₂) and calcium oleate (CaOl₂), added together (1/1) or separately

in linseed oil, it is possible that these results could vary slightly if the samples were prepared at fixed molar concentration; however, the synergy observed with the combination of Ca and Zn oleates is significant enough to be considered, despite the small difference in molar concentration listed in Table 1. Among the oil samples measured, no other combination of two metal carboxylates showed such strong synergistic tendency to shorten the drying time of linseed oil.

Interestingly, there seems to be a minimal threshold concentration of around 5 wt.% as the reduction of the drying time is not as significant when oil samples containing 2 wt.% of calcium and zinc oleates are used (Fig. 8).

Combinations of three and four metal carboxylates in linseed oil

Adding a third metal oleate (CaOl₂/ZnOl₂/CuOl₂ and CaOl₂/ZnOl₂/PbOl₂ oleates) did not result in significantly shortened drying rates. As it is clear from the overview in Fig. 7, the ensuing drying times were comparable to those of lead and copper oleates added separately in linseed oil. The combination of four metal oleates (CaOl₂/ZnOl₂/PbOl₂/CuOl₂) resulted in the shortest drying time among all oil samples characterised, with a reduction of the linseed oil drying time from 120 to 18 h when added in a mass concentration of 10 wt.% (0.038 M of CaOl₂,

0.037 M of ZnOl₂, 0.030 M of PbOl₂, and 0.037 of CuOl₂) (Fig. 9).

Viscosity measurements

As a complementary investigation, the viscosity of oil samples containing one and several metal carboxylates (stearates or oleates) was compared at equal shear rate (59 s⁻¹). As indicated in the overview of Fig. 10 the viscosity of the raw linseed oil, without addition of metal carboxylates, was measured to be 50 mPa·s at this shear rate.

One metal carboxylate in linseed oil

The results indicate that the addition of both single metal oleate and stearate renders the resulting medium significantly more viscous. At same shear rate, the viscosity increases as the mass percentage of metal oleates or stearates rises (Fig. 11). In most cases, the inclusion of 10 wt.% of Ca (0.153 M of CaSt₂ and 0.154 M of CaOl₂), Zn (0.147 M of ZnSt₂ and 0.148 M of ZnOl₂), Pb (0.121 M of PbSt₂ and 0.121 M of PbOl₂) and Cu (0.147 M of CuSt₂ and 0.149 M of CuOl₂) appears to (at least) double the viscosity, with Cu oleate and stearate resulting in the highest viscosity (141.3 mPa·s with 10 wt.% of Cu oleate and 130.3 mPa·s with 10 wt.% of Cu stearate) and Pb oleate in the lowest (89.3 mPa·s with 10 wt.% of Pb oleate). A general observation is that the addition of metal stearates to linseed oil increases the viscosity of

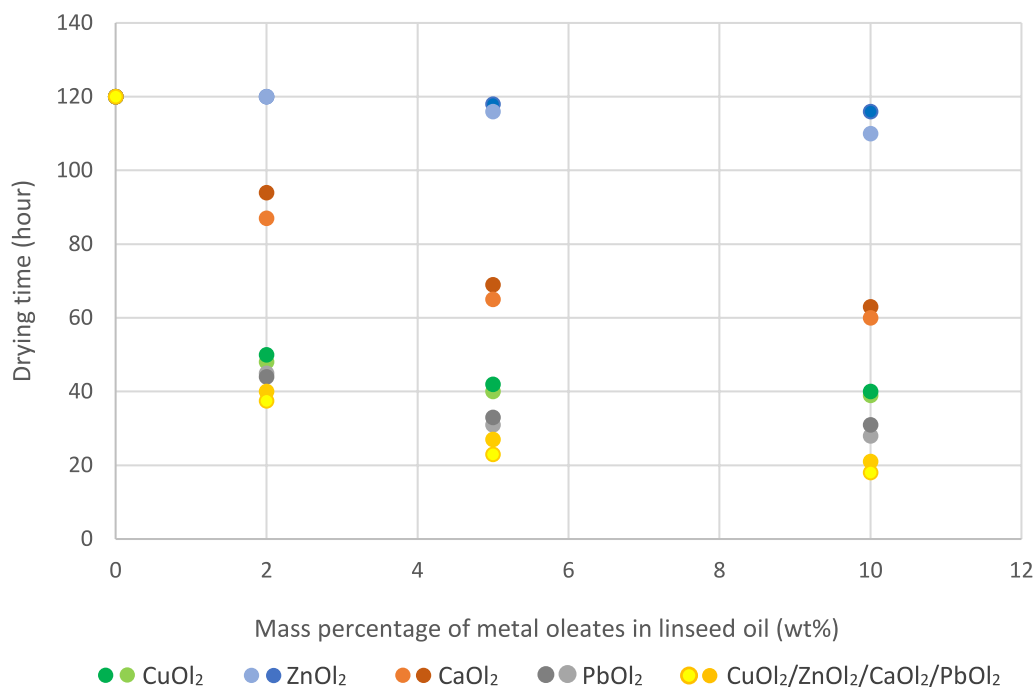


Fig. 9 Evolution of the drying time (hour) of linseed oil with an increasing concentration of zinc oleate (ZnO₂), calcium oleate (CaO₂), lead oleate (PbO₂), and copper oleate (CuO₂), added together (1/1/1/1) or separately

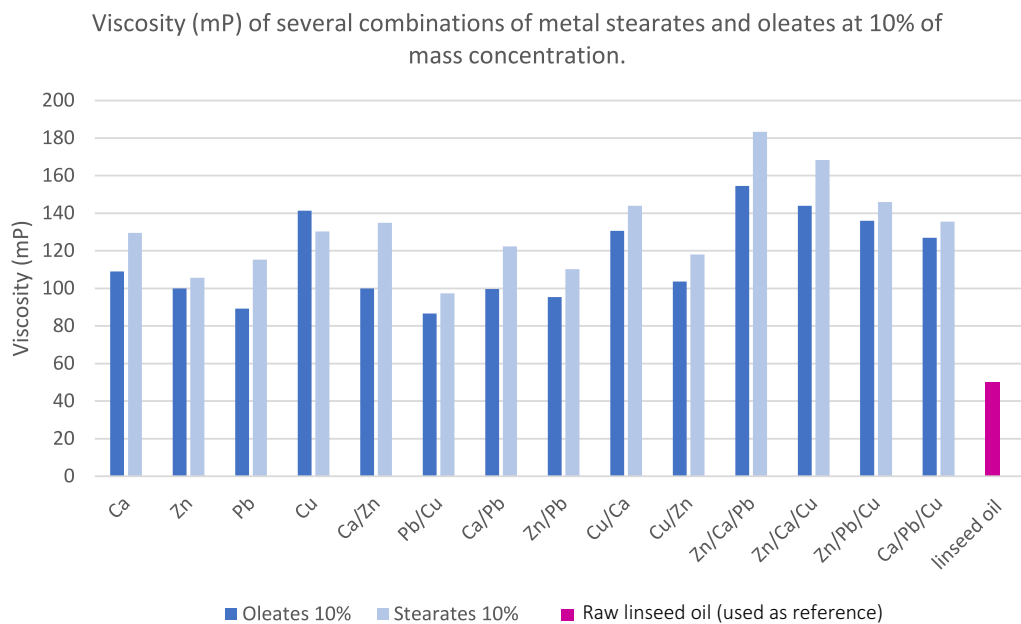


Fig. 10 Comparison of the viscosity of linseed oil containing either combinations of metal oleates or metal stearates, added in a mass concentration of 10%. Measurements were conducted at given shear rate of 59 s⁻¹

the resulting medium more than the addition of metal oleates, while the latter yield the shortest drying times. A notable exception is copper oleate, which resulted in the

highest viscosity (141.3 mPa·s) among the metal carboxylates tested individually.

The different influences of stearates and oleates on the viscosity are expected to be related to the structure of the

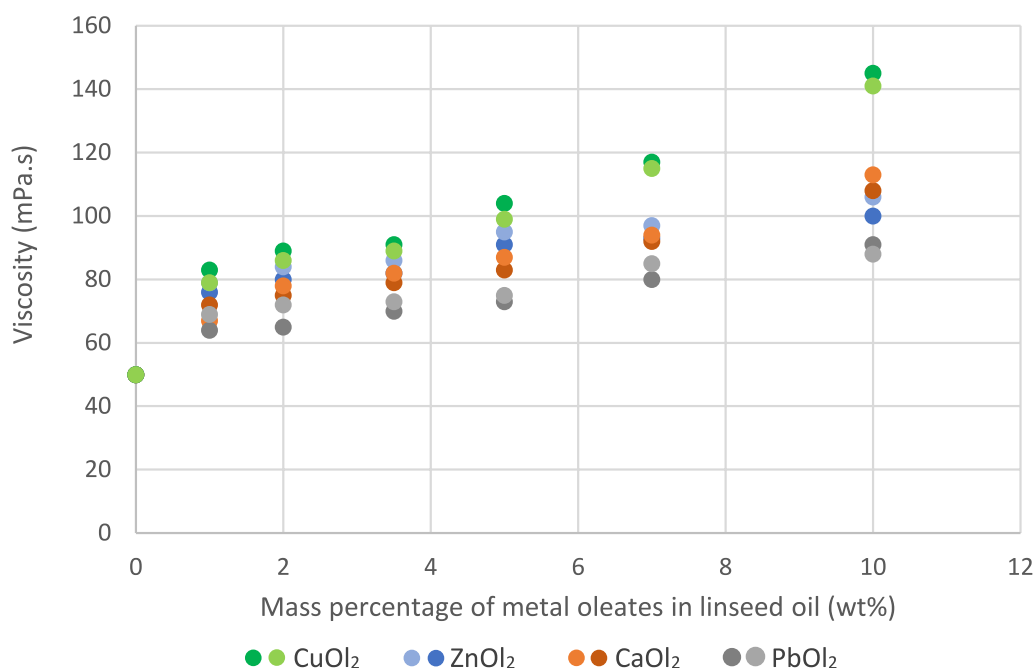


Fig. 11 Variation of the viscosity of linseed oil with increasing concentration of copper oleate (CuO₂), zinc oleate (ZnO₂), calcium oleate (CaO₂), and lead oleate (PbO₂), added separately

metal carboxylates in linseed oil. As the exact structure of the metal carboxylates in the oil samples has not been investigated at this stage of the research, valid hypotheses explaining these results cannot yet be proposed.

Combinations of two metal carboxylates in linseed oil

None of the combinations of two metal carboxylates (Ca/Pb, Ca/Cu, Cu/Pb, Zn/Pb, and Zn/Cu oleates and stearates) significantly enhanced the viscosity of the binder in comparison to the same metal carboxylates added separately in linseed oil. Unlike the results obtained with the drying measurements, the combination of Ca/Zn oleates (as well as the combination of Ca/Zn stearate) have not demonstrated any tendency to increase the viscosity of the binder (Fig. 12).

Combinations of three metal carboxylates in linseed oil

Starting from 3.5 wt.%, combinations of Ca/Zn/Cu (0.018 M of Ca, 0.017 M of Zn, and 0.017 M of Cu) and Ca/Zn/Pb (0.018 M of Ca, 0.017 M of Zn, and 0.014 M of Pb) oleates and stearates show a higher tendency to increase the viscosity of the binder than the same metal carboxylates added separately to linseed oil (Figs. 13 and 14). However, two other ternary combinations, Ca/Cu/Pb (0.018 M of Ca, 0.017 M of Cu, and 0.014 M of Pb) and Zn/Cu/Pb (0.017 M of Zn, 0.017 M of Cu,

and 0.014 M of Pb) oleates and stearates, did not show this effect. The former results do not correlate with the measurements of the drying times, as only combinations of two (Ca/Zn oleates) and four metal carboxylates (Ca/Zn/Pb/Cu oleates) demonstrated synergistic effects with respect to reducing the drying time.

According to these results, specific combinations of metal carboxylates appear efficient to increase the viscosity of the binder (at a shear rate of 59 s⁻¹) in comparison to when the same metal carboxylates are added separately. In particular, zinc and calcium oleates or stearates—added together with a third metal (copper- or lead-based) carboxylate—appear to interact, resulting in oil of a higher viscosity. Indeed, at the same mass percentage (starting from 3.5%), these combinations of metal carboxylates reach higher viscosities than the same metal carboxylates added separately in linseed oil. As observed with the measurements of the drying time, the results indicate that specific metal carboxylates can also act in synergy to increase the viscosity of the binder. Since different shear rates occur during the application and the drying of a paint layer (e.g. the shear rate exerted by brushing varies from 1000 to 35,000 s⁻¹), viscosity measurements at other shear rates should be conducted to have a more complete overview of the flow properties of each oil sample [22, 37–41].

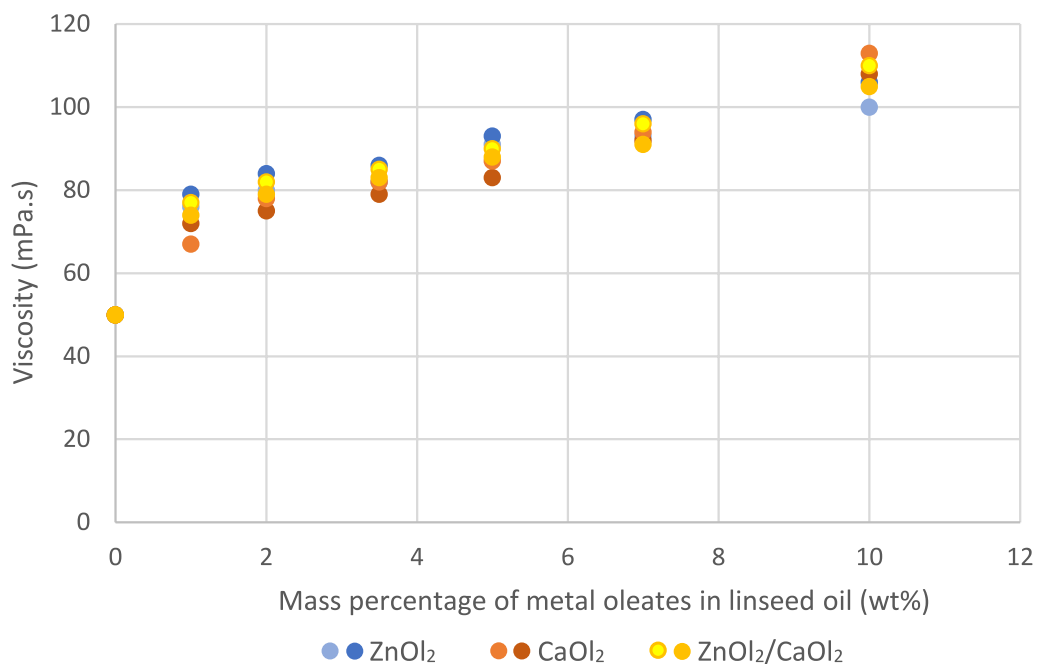


Fig. 12 Variation of the viscosity of linseed oil with an increasing concentration of zinc oleate (ZnOl₂) and calcium oleate (CaOl₂), added together (1/1) or separately

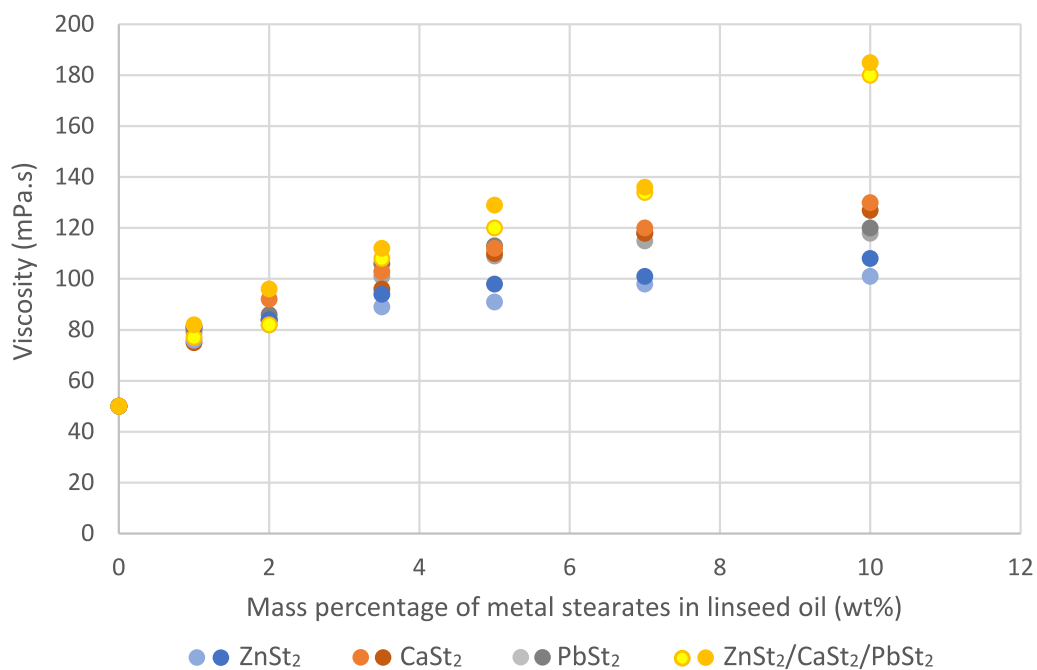


Fig. 13 Variation of the viscosity of linseed oil with an increasing concentration of calcium stearate (CaSt₂), zinc stearate (ZnSt₂), and lead stearate (PbSt₂), added together (1/1/1) or separately

Conclusions

The results of this research show that specific combinations of metal carboxylates reduce the drying time

of the oil binding medium and/or increase its viscosity (at low shear rate) more efficiently than each metal carboxylate added separately in linseed oil. In particular,

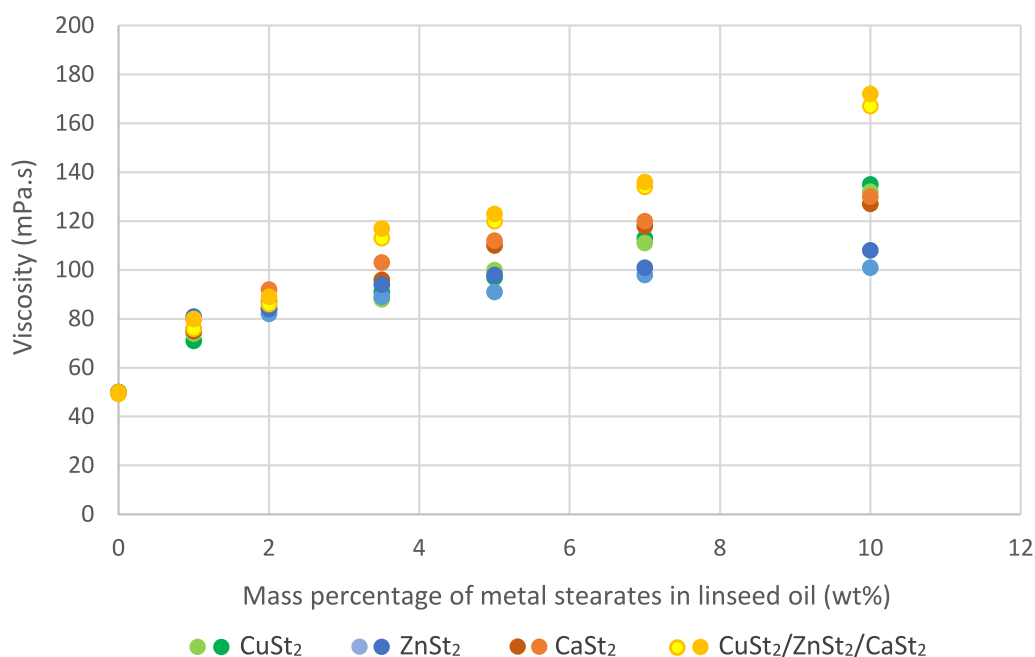


Fig. 14 Variation of the viscosity of linseed oil with an increasing concentration of copper stearates (CuSt₂), zinc stearate (ZnSt₂), and calcium stearate (CaSt₂), added together (1/1/1) or separately

combinations of Ca/Zn oleates proved to be particularly efficient in accelerating the drying of the binder; however, none of the binary metal carboxylates combinations demonstrated any synergistic effect towards modifying the viscosity. Adding a third metal carboxylate was also found to be quite effective; associations of three metal carboxylates containing calcium, zinc and copper or lead carboxylates have shown the best results towards increasing the viscosity of the binder. For the drying time, the combination of four metal oleates (Ca/Zn/Cu/Pb oleates) proved to be particularly efficient, reducing the drying time of the binder to around 18 h compared to 120 h for raw linseed oil. These results demonstrated that when added in judicious combinations, specific metal carboxylates may act in synergy to improve their impact on the drying and the viscosity of the binder. The demonstration of synergistic effects with specific associations of metal carboxylates in linseed oil is an interesting and relevant outcome, as it contributed to our understanding of the painting materials employed by the Van Eyck brothers when creating the *Ghent Altarpiece*. Based on this investigation, it seems plausible that a high-quality oil paint binder, with a short drying time and suitable handling properties, results from the modification of linseed oil by heating with the addition of small amounts of metal salts that promote the formation of several metal carboxylates. Nevertheless, it must be pointed out that

further investigations are needed to study the mechanism of this synergistic effect, by characterising the exact structure of the metal carboxylates in the model samples. Monitoring the modification of the oil samples containing synthesised carboxylates by FTIR spectroscopy, at constant temperature and relative humidity, is envisaged to follow this preliminary investigation.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-024-01309-y>.

Supplementary material 1.

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Author contributions

All authors contributed to data interpretation and to finalising the manuscript. All authors have read and approved the final manuscript.

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Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests

The authors declare that they have no competing interests.

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