

Chapter 9

Factors Affecting the Reactivity of Zinc Oxide with Different Drying Oils: A Vibrational Spectroscopy Study



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Abstract This study focuses on the short-term reactivity of zinc oxide with different types of drying oils. Chemical grade zinc oxide (with diameter <100 nm) was mixed with oils with different proportions and types of fatty acids. Specifically, reactivity of zinc oxide with alkali-refined linseed oil, raw linseed oil, boiled linseed oil, polymerized linseed oil, stand oil, tung oil, and alkyd was studied between 4 days and 10 months. Effects of short-term exposure to temperature, humidity, and pH were also evaluated. The type of metal soaps formed and the kinetics of formation were monitored with attenuated total reflection Fourier transform infrared (ATR- FTIR) spectroscopy. The results confirm that humidity and heat combined favor the formation of both network-coordinated zinc carboxylates (POL-Zn) and zinc complexes of free fatty acids (FA-Zn) irrespective of the type of oil; however, the phenomenon is particularly severe for alkali-refined, raw, and boiled linseed oils, while stand oil and tung oil show the lowest amounts of zinc soap (FA-Zn) formation. The findings advance our knowledge of the reactivity of zinc oxide with an expanded range of drying oils that are commonly encountered in many nineteenth- and twentieth-century paints and reinforce the notion that even short-term exposure to heat with humidity can have irreversible effects on zinc carboxylate formation.

Keywords Zinc carboxylates · Drying oils · ATR-FTIR · Artificial aging · Humidity · Linseed oil · Tung oil · Stand oil · Alkyd

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9.1 Introduction

9.1.1 *Historical Perspectives from Paint Technology Manuals*

Zinc oxide is a common white pigment in paints that were formulated in the nineteenth and twentieth centuries. In-depth studies of technical manuals on the early twentieth-century paint-making technology uncovered frequent passages seeming to imply that promoting the reaction of zinc oxide with the paint medium would lead to superior quality enamels (Kokkori et al. 2014a, 2015b). Recommendations for “exceptionally high-grade” enamels included preparing a paste with an excess of zinc white (obtained, e.g., by grinding 65 pounds of condensed zinc white in 28 pounds of heavy oil and 7 pounds of pure turpentine) and letting the paste stand for at least a week, before adding to it 60 pounds of varnish made from pale kauri gum and linseed oil (Mattiello 1943; Kokkori et al. 2014b). Other authors recommended setting away the paste of zinc oxide with medium – often a thermally treated, bodied oil – “to ripen” in closed containers for at least 2 weeks or even longer, before reducing this “white enamel base” with varnish or other diluents to the desired consistency (Uebele 1913). Among those early oil-based enamels are the ones produced by the French brand Ripolin, which had an important role among the materials used by the global artistic avant-gardes and was notably used by artists such as Pablo Picasso (1881–1973), Francis Picabia (1879–1953), and others (Gautier et al. 2009; Muir et al. 2013; Dredge et al. 2013; McMillan et al. 2013; Kokkori et al. 2015a). Interestingly, when studied under the scanning electron microscope, these Ripolin paints show very even dispersion of the pigment particles, much more so than zinc oxide-containing fine artist paints from tubes (Muir et al. 2011). This observation suggests that paint makers might have included those recommendations because of empirical knowledge that the early formation of complexes of zinc ions with fatty acids from the oil would act as an internally formed dispersant, avoiding the clumping of pigment particles. The historical literature thus provided the inspiration for the present study, which focused on the short-term reactivity of zinc oxide with an expanded range of oils, beyond linseed oil alone, which are commonly encountered in industrial and artist’s paint manufacture.

9.1.2 *Experimental Studies*

Previous studies of zinc-based carboxylates (Fauve and Vandenmaele 1964; Robinet and Corbeil 2003; van der Weerd et al. 2005; Barman and Vasudevan 2007; Rogala et al. 2010; Osmond et al. 2012; Hermans et al. 2015) have shed light on the organic/inorganic compounds that form by reaction of the zinc oxide pigment with the lipidic binding medium, identifying mostly zinc palmitates ($\text{Zn}(\text{C}_{16})_2$), stearates ($\text{Zn}(\text{C}_{18})_2$), and oleates ($\text{Zn}(\text{C}_{18:1})_2$) in crystalline and amorphous states (for brevity,

the abbreviation FA-Zn is going to be used to identify this class of zinc complexes of free fatty acids). Most recently, it has been convincingly proposed that soaps whose FTIR spectra cannot be correlated to that of a specific type of zinc carboxylate (Robinet and Corbeil 2003; Otero et al. 2014) may consist of network-coordinated zinc soaps, i.e., zinc carboxylate moieties that are covalently bonded to the cross-linked and cured oil (Hermans et al. 2015, 2019; Hermans 2017) (these will hereafter be called POL-Zn). Fourier transform infrared analysis in transmittance of many Ripolin paints has demonstrated that these oil-based enamels have spectra with characteristic broad antisymmetric vibrations of the carboxylate group, centered at approximately 1585 cm^{-1} , which have been attributed to such network-coordinated zinc soaps (Gautier et al. 2009; Muir et al. 2013; McMillan et al. 2013) (POL-Zn). It is interesting to highlight that many paintings believed to be made with Ripolin (some nearing 100 years of age) have been proven to be stable and have not shown characteristic zinc soap protrusions (Casadio et al. 2013; Muir et al. 2013; McMillan et al. 2013) as have been otherwise observed in zinc oxide-containing paints by, for example, Vincent van Gogh (van der Weerd et al. 2003), or delamination of paint as noted for paintings by Piet Mondrian (Raven et al. 2019), abstract expressionist painters (Rogala et al. 2010), and others. It should be noted that it is the crystalline zinc soaps (FA-Zn), which are found in protrusions and at the interface of paints that are delaminating.

In recent years, the deterioration phenomena associated with the reaction between the metal ions of the pigment and the organic matrix have become a major concern for art conservators and the scientists interested in unraveling the chemical processes, crystallization, and kinetics of metal soap formation, as the many chapters in this volume attest. Surprisingly, while our knowledge of metal soaps has significantly advanced in the past 20 years overall, comparably little work has been done on the early stages of formation of zinc soaps. In 2012 Clementi et al. (Clementi et al. 2012) studied Gamblin alkyd medium and linseed oil mixed with zinc oxide (1:2 wt) aged in the dark at $40\text{ }^{\circ}\text{C}$ and 95% RH. FTIR spectra taken at 15, 28, 50, 69, and 88 days demonstrated how, when plotting the ratio of the intensity of the FTIR $\nu\text{C}=\text{O}$ band of the lipidic component of the oil at 1730 cm^{-1} versus the antisymmetric COO^- stretching of newly formed metal carboxylates at 1600 cm^{-1} , the ratio became stable after 15 days of aging. No data was offered before day 15 though, while the historical technical manuals discussed previously clearly seem to indicate reactivity after a few days. Poli and coworkers performed artificial aging of mixtures of Kremer zinc oxide and shellac 1:1, aged for 3 minutes at $300\text{ }^{\circ}\text{C}$ on a heating plate, which led to the formation of disordered or network-coordinated zinc carboxylates with resinous acids (as indicated by the observation of the broad FTIR band at 1585 cm^{-1}) (Poli et al. 2014). As described in this volume (Poli et al. 2019) 1000 h of UV aging in a solar box (cutting $\lambda < 300\text{ nm}$) of the same mixture led to the formation of zinc oxalates. Finally, Hermans et al. (Hermans et al. 2015; Hermans 2017) explored the reactivity of mixtures of cold-pressed linseed oil with zinc oxide with and without the addition of demineralized water (to promote soap formation) stirred in a sealed vial at room temperature (RT) for 3 days, then pipetted

on a glass slide, and left to dry for 7 weeks, leading to the observation of POL-Zn after a week of curing.

Despite these previous efforts, a systematic study is lacking, focusing on the early-stage reactivity of zinc oxide with an expanded range of drying oils commonly encountered in many nineteenth- and twentieth-century paints. This work aims at filling that gap, by concentrating on the short-term reactivity of zinc oxide and evaluating the effect of the type of oil used. Variables examined included the drying oil's viscosity, degree of prepolymerization, availability of free fatty acids in the initial oil composition (as expressed by their acid value, when available from the manufacturer), and type of free fatty acids contained in the TAGs (triacylglycerides). Specifically, four variously processed linseed oils were used, whose free fatty acid values were provided by the manufacturer, ranging from 0.3 max for alkali-refined linseed oil to 19 max for polymerized linseed; these were chosen to explore whether the initial availability of different amounts of free fatty acids is a factor in the short-term formation of zinc carboxylates and their evolution over time. Bodied oils (polymerized linseed, boiled linseed, and stand oil) were also examined, to evaluate the effect of higher viscosity (when compared to unbodied oils) and prepolymerization on the formation of zinc carboxylates. Finally an oil-based alkyd medium containing 10–20% of safflower oil (which has higher proportions of linoleic but lower proportions of linolenic acid than linseed oil) as well as tung oil (which is very rich in the triply unsaturated conjugated α -eleostearic C18:3 oil) (see Table 2.1 in Osmond 2019) was included to explore the effects of different oil chemistries. Additionally, the effect of short-term exposure to high levels of humidity coupled with elevated temperature as it could be experienced by painted surfaces during treatments such as paint consolidation, flattening, and relining were explored. Lastly, the effect of low pH was also evaluated. The type of metal soaps formed and the kinetics of formation were monitored with ATR-FTIR.

9.2 Materials and Methods

9.2.1 Paint Mixtures

Paints were prepared by hand-mixing with a spatula on a glass slide zinc oxide particles with oil in proportions of 2:1 (v:v) pigment-binder until a viscous, stringy consistency was obtained, which mimicked paint formulations as they would be used by artists. Chemical grade zinc oxide (Sigma-Aldrich) of diameter smaller than 100 nm (as certified by the manufacturer) was used. Because chemical grade zinc oxide is of significantly smaller particle size, and larger surface area than pigment grade, it has been shown to be substantially more reactive than artists' pigment in previous models (Osmond 2014). Therefore it should be expected that reaction products will be formed in a shorter timescale than if experiments were conducted using artist grade zinc oxide.

Several different commercial oils were used; where available, their industrially determined acid value (a measure of the free fatty acids available in the oil (Bailey 1951)) is indicated in parenthesis. These were alkali-refined linseed oil (Welch, Holme and Clark, Inc. (WHC), acid value 0.3 max), raw linseed oil (Alnor, acid value 4 max), boiled linseed oil (WHC, acid value 7.5 max), polymerized linseed oil (Alnor, K-6 grade, acid value 19 max), stand oil (Winsor and Newton), tung oil (WHC, acid value 5 max), and alkyd (Gamblin Galkyd slow dry, certified by the manufacturer to contain 40–60% of alkyd resin and 10–20% safflower oil). Immediately after mixing, a small quantity of each different paint was deposited on a microscope cover glass in the form of a 6-mm-diameter drop of paint of approx. 0.8–1 mm thickness in preparation for artificial aging, while a set of all paint mixtures was left to rest in the dark, at laboratory ambient conditions ($T = 20\text{ }^{\circ}\text{C} \pm 2$ and $\text{RH}\% = 50 \pm 5$).

9.2.2 *Conditions of Artificial Aging*

After mixing, samples were left for 2 days at room temperature before being subjected to the artificial aging regimen described below for 2 days. The short, 48-h aging time was chosen to simulate the effect of a conservation treatment such as lining, consolidation or flattening of paint, which would have a short duration, though it should be noted that at such early stages of curing, some paints were not even touch-dry yet.

Paint mixtures were aged (1) at room temperature (RT in the following), (2) in a dry oven at 80°C (labeled 80 in the following), and (3) at 80°C in a sealed glass jar containing a small beaker where the samples were positioned, surrounded by a saturated solution of KNO_3 (Sigma-Aldrich) to ensure approximately 90% RH (called 80+RH). In a subset of these glass jars, (4) a small vial containing a saturated solution of oxalic acid dihydrate (Sigma-Aldrich) was added to the chamber to simulate an acidic and humid environment (termed 80+RH+H+ in the following). In both of the latter cases, a Gore-Tex membrane was affixed to the top of the beaker with the paint samples to avoid direct condensation of water onto the paint surfaces (Fig. 9.1).

After the 2 days at RT and 2 days of heating in the conditions described above, all samples were removed from the glass jars and left in the dark at room temperature.

9.2.3 *Instrumentation*

A Bruker Alpha small footprint portable FTIR spectrometer with ATR module with diamond crystal was used to monitor the samples. A small amount of paint (in the form of a chip measuring approximately 2×2 mm and 0.5–0.8 mm in thickness) was placed on the diamond crystal face, and, upon applying a consistent

Fig. 9.1 The sealed glass jar used for aging paint mixtures with hot, humid, and acidic air (80+RH+H+). The jar diameter is 8 cm



pressure with the instrument's anvil, 64 scans were acquired at a resolution of 4 cm^{-1} between 4000 and 400 cm^{-1} . Care was taken in making sure that it was always the uppermost portion of the sample (the one in contact with the atmosphere during aging) to be in direct contact with the ATR crystal. The depth of penetration (optical path length) inside the surface of the sample in contact with a diamond crystal is estimated by the manufacturer to be $1.66\text{ }\mu\text{m}$ at 1000 cm^{-1} and with a 45° incidence. The spectra illustrated here represent an average of three measurements for each sample.

The first ATR-FTIR measurements were conducted after 4 days, inclusive of 2 days at room temperature immediately after mixing, and 2 days under the respective regime of artificial aging. Subsequently, all samples were left at room temperature and measured with the ATR-FTIR after 10 months. A subset of samples was also measured at 21 days (Table 9.1).

To account for the different degrees of coverage and contact with the diamond crystal by the samples (especially at 4 and 21 days, as some samples were still jelly-like, whereas others were completely hardened) and in order to achieve a consistent comparison of the formation of different metal carboxylate species, the following procedure was used.

All spectra were normalized by the intensity of the CH stretch at around 2922 cm^{-1} , which can be considered to remain fairly constant under the conditions used. Then maximum band intensity was calculated with the OPUS 7 software after subtraction of the baseline for the $\nu\text{C}=\text{O}$ ester band of the oil at $1741\text{--}38\text{ cm}^{-1}$ (labeled I_{1740} in the following), as well as the antisymmetric COO^- stretching of newly formed network-coordinated metal carboxylates (POL-Zn) at 1585 cm^{-1} (I_{1585}) and of the sharp band at $1540\text{--}50\text{ cm}^{-1}$ (I_{1540}) of crystalline metal soaps (FA-Zn) (Table 9.1). This method has limitations, because even after subtraction of the baseline and normalization, the maximum peak intensity of convoluted or

Table 9.1 Normalized band intensities for FTIR peaks characteristic of the ν_{CO} of the oil and the ν_{asCOO^-} of newly formed carboxylates (FA-Zn and POL-ZN) for the oil and zinc oxide mixtures studied under the different aging regimes

Oil	Acid value	Condition	10 months						21 days						4 days									
			I(1740)		I(1585)		I(1540)		I(1540)/I(1585)		I(1740)		I(1585)		I(1540)/I(1585)		I(1740)		I(1585)		I(1540)/I(1585)			
			I(1740)	I(1585)	I(1540)	I(1585)	I(1540)	I(1585)	I(1540)/I(1585)	I(1740)	I(1585)	I(1540)	I(1585)	I(1540)/I(1585)	I(1740)	I(1585)	I(1540)	I(1585)	I(1540)/I(1585)	I(1740)	I(1585)	I(1540)	I(1585)	I(1540)/I(1585)
Alkali-refined linseed	0.3 max	RT	1.25	0.64	N/A	N/A	N/A	N/A											1.36	N/A	N/A	N/A	N/A	
		80	1.46	0.23	N/A	N/A	N/A	N/A	1.52	0.41	N/A	N/A	N/A						1.21	0.13	N/A	N/A		
		80+RH	0.48	0.31	0.95	3.08														0.77	0.50	0.58	1.16	
		80+RH+H+	0.49	0.41	0.92	2.23	0.52	0.33	0.79	2.42										0.88	0.64	0.76	1.20	
Raw linseed	4 max	RT	1.30	0.50	N/A	N/A	N/A	N/A											1.37	N/A	N/A	N/A	N/A	
		80	1.56	0.20	N/A	N/A	N/A	N/A	1.52	0.13	N/A	N/A	N/A						1.57	0.09	N/A	N/A		
		80+RH	0.59	0.52	0.86	1.67														0.77	0.50	0.58	1.16	
		80+RH+H+	0.52	0.40	0.87	2.20	0.51	0.39	0.90	2.28										0.88	0.64	0.76	1.20	
Boiled linseed	7.5 max	RT	1.47	0.53	N/A	N/A	N/A	N/A											1.21	N/A	N/A	N/A	N/A	
		80	0.91	0.17	N/A	N/A	N/A	N/A	1.41	0.22	N/A	N/A	N/A						1.57	0.21	N/A	N/A		
		80+RH	0.60	0.44	0.75	1.70														0.79	0.53	0.67	1.26	
		80+RH+H+	0.75	0.53	0.70	1.33	0.47	0.25	0.91	3.69										0.77	0.48	0.53	1.09	
Polymerized linseed	19 max	RT	1.24	0.27	N/A	N/A	N/A	N/A											1.17	N/A	N/A	N/A	N/A	
		80	1.11	0.10	0.11	1.16	1.10	0.08	N/A	N/A									1.13	0.08	N/A	N/A		
		80+RH	0.55	0.21	0.64	3.07														0.76	0.34	N/A	N/A	
		80+RH+H+	0.48	0.20	0.61	3.00	0.58	0.26	0.55	2.15										0.77	0.34	N/A	N/A	

(continued)

Table 9.1 (continued)

Oil	Acid value	Condition	10 months						21 days						4 days					
			I(1740)		I(1585)		I(1540)/I(1585)		I(1740)		I(1585)		I(1540)/I(1585)		I(1740)		I(1585)		I(1540)/I(1585)	
			I(1740)	I(1585)	I(1540)	I(1585)	I(1540)/I(1585)	I(1740)	I(1585)	I(1540)	I(1585)	I(1540)/I(1585)	I(1740)	I(1585)	I(1540)	I(1585)	I(1540)/I(1585)	I(1740)	I(1585)	I(1540)
Stand oil		RT	1.24	0.14	N/A	N/A	N/A									1.20	N/A	N/A	N/A	N/A
		80	1.20	0.09	N/A	N/A	N/A	1.20	0.07	N/A	N/A					1.23	0.06	N/A	N/A	N/A
		80+RH	0.89	0.30	0.38	1.26										0.97	0.19	N/A	N/A	N/A
		80+RH+H+	0.94	0.23	0.26	1.13		0.99	0.26	1.09						0.98	0.18	N/A	N/A	N/A
Tung oil		RT	1.92	N/A	N/A	N/A										1.39	N/A	N/A	N/A	N/A
		80	1.86	N/A	N/A	N/A	1.71	N/A	N/A							1.70	N/A	N/A	N/A	N/A
		80+RH	1.25	0.36	0.34	0.95										1.21	0.41	N/A	N/A	N/A
		80+RH+H+	1.25	0.34	N/A	N/A	1.11	0.53	N/A	N/A						1.17	0.48	N/A	N/A	N/A
Galkyd		RT	1.98	0.48	N/A	N/A										1.89	0.17	N/A	N/A	N/A
		80	1.91	0.48	N/A	N/A	2.25	0.38	N/A	N/A						2.19	0.30	N/A	N/A	N/A
		80+RH	1.75	0.80	0.97	1.21										1.72	0.47	N/A	N/A	N/A
		80+RH+H+	1.66	0.82	1.11	1.35		1.66	0.82	0.98						1.68	0.74	0.91	1.22	

N/A indicates that a band was not observed; when a space is left blank, it means that the measurement was not carried out

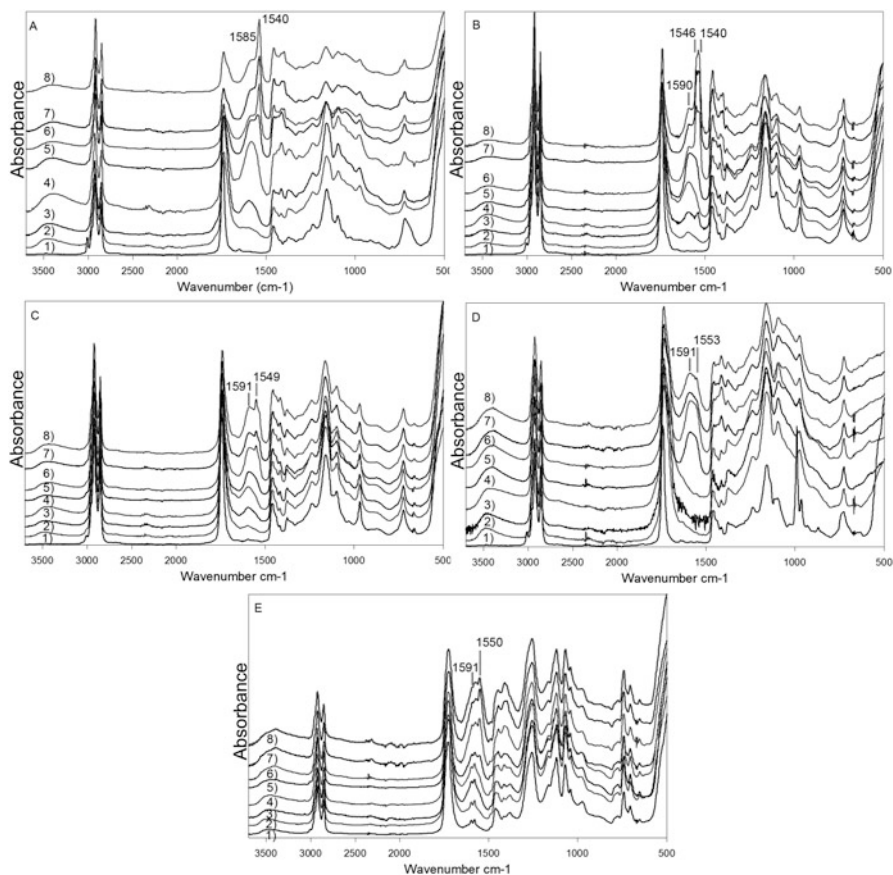


Fig. 9.2 ATR-FTIR spectra of paint mixtures of zinc oxide with (a) alkali-refined linseed oil; (b) polymerized linseed oil; (c) stand oil; (d) tung oil; (e) Galkyd, at various stages of aging, specifically (1) RT 4 days; (2) 80 4 days; (3) 80 10 months; (4) RT 10 months; (5) 80+RH 4 days; (6) 80+RH+H+ 21 days; (7) 80+RH+H+ 10 months; (8) 80+RH 10 months

overlapping bands (such as the sharp 1540 cm^{-1} band, which overlaps with the broad band at 1585 cm^{-1}) is difficult to calculate precisely due to the reciprocal contributions of overlapping bands. As a result, in this work the intensity of the peak at 1540 cm^{-1} has been marked only when a sharp peak was discernible. Though in such cases complete spectral decomposition and calculation of the area below each individual peak is preferable, comparison of band intensity is a rapid method of evaluation that has been employed by other authors (Clementi et al. 2012) to provide a reliable qualitative visualization of trends for chemical change as reflected in infrared spectra.

All spectra were also corrected to remove any residual water vapor and CO_2 absorptions (atmospheric compensation of the OPUS software). In Fig. 9.2, all spectra are normalized by the intensity of the CH stretch at around 2922 cm^{-1} , for ease of comparison.

9.3 Results and Discussion

Plotting the intensity of the characteristic band for POL-Zn (I_{1585}) and comparing it with that of FA-Zn (I_{1540}), as illustrated in Fig. 9.3, demonstrate that POL-Zn were not yet detectable with ATR-FTIR after 4 days of aging at RT, with the exception of the Galkyd medium, but that POL-Zn had already formed after 4 days for all the samples exposed to heat and humidity. Furthermore, alkali-refined, raw linseed, and boiled linseed oil showed formation of FA-Zn upon exposure to hot and humid conditions (80+RH). The Galkyd showed a similar trend while the heavily bodied oils such as polymerized linseed and stand oil, and the quick-drying tung oil showed no formation of FA-Zn after 4 days both at RT and 80+RH.

Figure 9.4 shows consistent trends over time, i.e., the development of FA-Zn after 10 months for all samples exposed to heat and humidity, a phenomenon that was not apparent immediately after 4 days but started being observed at 21 days and continued to evolve. Over time (Fig. 9.4 and Table 9.1), no oils showed formation of FA-Zn unless they were exposed to the high humidity combined with high-temperature aging regimen (80+RH or 80+RH+H+).

Lowering the pH of the hot and humid air in some cases caused higher overall formation of zinc carboxylates, but in general, as evident from Table 9.1, the effects of the 80+RH+H+ regime were comparable (within the uncertainty of the measurement) to the 80+RH samples.

The trends illustrated in Figs. 9.3 and 9.4 also demonstrated that the amount of free fatty acids initially available in the oil used, as determined through their reported acid value, was not a good predictor of the propensity of a certain oil to form POL-Zn or FA-Zn when mixed with the pigment. To the contrary, the three oils with the lowest reported acid value (alkali-refined, raw, and boiled linseed) appeared

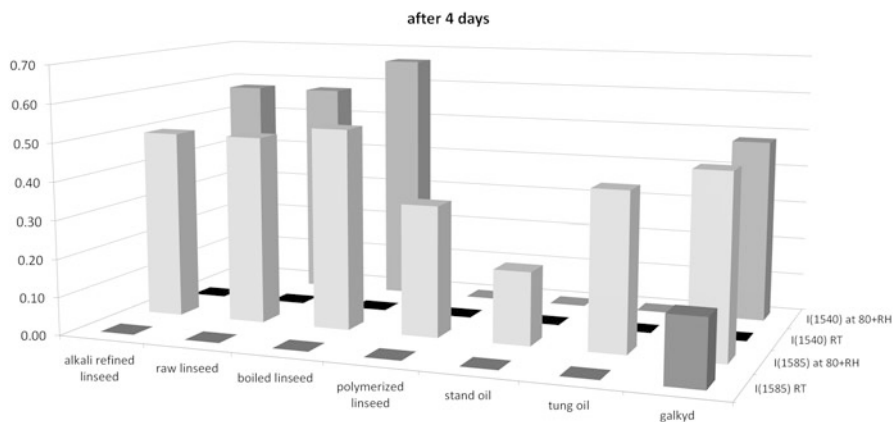


Fig. 9.3 Visualization of the values of I_{1585} and I_{1540} after 4 days of aging in two conditions: RT and 80+RH (for a full list of measured values, see Table 9.1; where a band intensity value is not plotted, it means that the band was not observed)

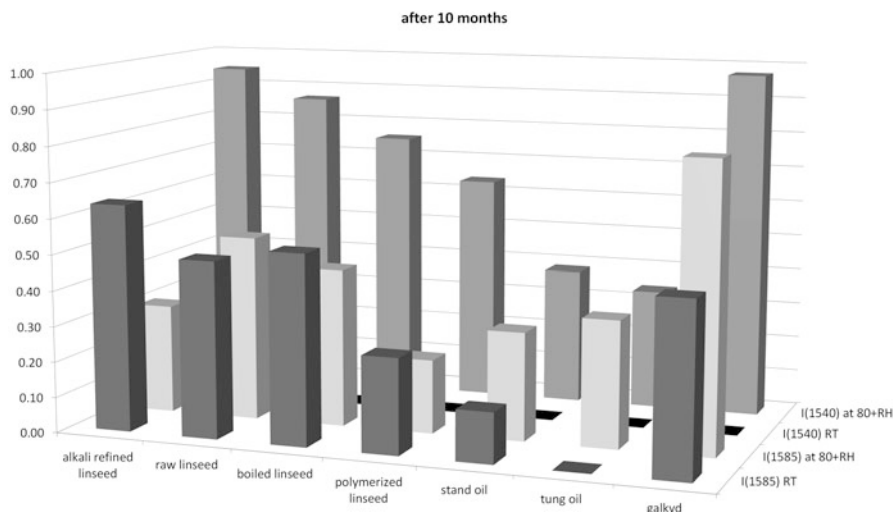


Fig. 9.4 Visualization of the values of I_{1585} and I_{1540} after 10 months of aging in two conditions: RT and 80+RH (for a full list of measured values, see Table 9.1; where a band intensity value is not plotted, it means that the band was not observed)

to form the highest amounts of FA-Zn both at 4 days and 10 months when exposed to 80+RH or 80+RH+H+ conditions. The same applied to the Galkyd (though its acid value was not known). Could it be that the highest amount of free fatty acids originally present in oils, such as the polymerized linseed oil, causes the zinc oxide particles to be “passivated” by a monolayer of free fatty acids, which, though hardly detectable by FTIR (Hermans et al. 2015), could render the Zn ions less available for reaction with the oil at later stages of curing? This hypothesis would nevertheless need to be experimentally demonstrated. The accuracy of the oil acid values provided by the manufacturers also requires verification.

After 4 days at 80+RH or 80+RH+H+, values of I_{1585} are similar for alkali-refined, raw linseed, and boiled linseed oils; however the polymerized linseed oil, one of the four linseed oils with the highest acid value reported, was the one that formed the lowest amount of POL-Zn and no FA-Zn after 4 days.

Alkali-refined linseed and raw linseed behaved in very similar ways, even though they had 0.3 max and 4 max free acid values reported. Together with the Galkyd, they are the media that developed the highest amount of POL-Zn at RT after 10 months of aging (Fig. 9.4).

Looking at these trends over time, it thus seems that viscous (bodied) oils such as polymerized linseed and stand oil have a lower tendency to form zinc carboxylates, perhaps due to issues of lower mobility of the carboxylic groups that are part of the polymer network and other transport phenomena in paints affecting both zinc ions and free fatty acids. The prepolymerization of these oils is also expected to affect their reactivity with the Zn particles. Further mechanistic studies should be conducted to explore this hypothesis further.

Overall, tung oil and stand oil were the least prone to forming zinc carboxylates (POL-Zn and FA-Zn) in the conditions used for this study. Because tung oil is very rich in the triply unsaturated conjugated α -eleostearic C18:3 oil and has much lower proportions of saturated and monounsaturated fatty acids with respect to linseed oil, its fast autoxidation and cross-linking, quickly leading to a hard and cured film, could be one of the reasons for its low tendency to form FA-Zn even at 80+RH.

Examining more specifically the spectra recorded for the different types of oils, several interesting observations can be made (Fig. 9.2). So as to keep the focus of this contribution on zinc carboxylate formation only, it should be noted that, in the discussion of the spectra, the phenomena of carbonyl band broadening and variations in the CH stretching bands that are related to the known processes of aging of the oil binding medium are not addressed, as they are already widely discussed in the literature (Meilunas et al. 1990; Lazzari and Chiantore 1999).

One interesting observation that is consistent for all samples studied (Fig. 9.2 and Table 9.1) is that 10 months after mixing, the amount of POL-Zn detected was actually higher for the samples aged at RT than the ones aged in dry oven at 80 °C. Though the exact reasons for this phenomenon are still under study, this finding further corroborates the limitations of dry heating as an artificial aging regime for oil paints that has also been demonstrated by other researchers (Erhardt et al. 2000). Dry heating alone, even at the relatively mild artificial aging regime of 80 °C and with exposures of only 2 days, initially seemed to accelerate aging. This was demonstrated by the formation of a small amount of POL-Zn after 4 days at 80 °C, which was not observed for the samples aged at RT. However, in the longer term, this study provided evidence that an aging regimen involving only heating at 80 °C will not cause the same type of chemical processes that are observed with natural aging.

For alkali-refined linseed oil (acid value 0.3 max), 4 days after mixing, at RT, there was no evidence of soap formation, while with heating and humid air, two main soaps bands are formed: a broad band approximately centered at 1585 cm^{-1} and a sharp one at $1550\text{--}51\text{ cm}^{-1}$. After 21 days, the 80 and 80+RH+H+ samples showed no substantial increase in the POL-Zn formed (indicated by the broad band at 1585 cm^{-1}). Rather, in the 80+RH+H+ samples at 21 days and 10 months, there was a great increase in the intensity of the 1540 cm^{-1} band (shifting to lower wavenumbers from the initially observed value of 1550 cm^{-1} after 4 days). These trends were rendered evident when observing the variation of intensity of the three bands (I_{1540} , I_{1585} , and I_{1740}) over time for samples of the different oils aged in the same conditions (80+RH+H+) and measured at different times (Fig. 9.5). The hydrolysis of the ester bonds of the oil over time was signaled by the decrease in I_{1740} , especially evident for alkali-refined and polymerized linseed, while the normalized I_{1740} remained fairly constant over time for Galkyd, tung, and stand oil. A decrease or fairly constant value of the POL-Zn species was also observed; specifically, I_{1585} decreased over time for alkali-refined, polymerized, and tung oil, while it showed a mild increase for Galkyd and stand oil. After initial formation at 4 days, the formation of FA-Zn species increases for all oils, except stand oil, for which a peak at 1540 cm^{-1} was detected after 21 days and 10 months (Fig. 9.2).

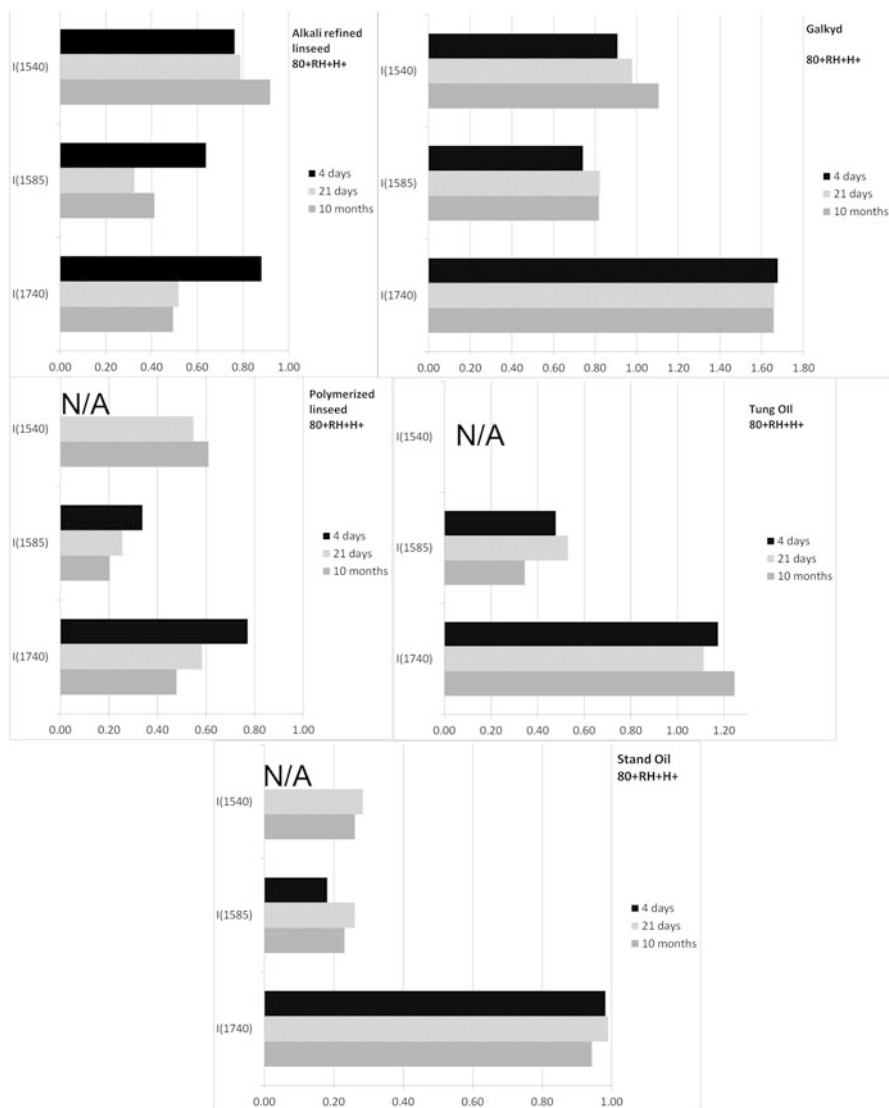


Fig. 9.5 Evolution over time of the normalized ATR-FTIR band intensities I_{1740} , I_{1585} , and $I_{1540-50}$ for the various oils studied at 80+RH+H+ (for a full list of measured values, see Table 9.1)

The tung oil did not show a distinctive peak at 1540 cm^{-1} in this aging regime, only a shoulder on the broad band centered at 1585 cm^{-1} , as illustrated in Fig. 9.2.

The spectra for polymerized linseed oil (Fig. 9.2) were unique in this group, because at 21 days, the 80+RH+H+ sample showed peaks at 1547 and 1532 cm^{-1} , with possibly a convoluted 1540 cm^{-1} contribution, becoming significantly more

intense than the broad absorption at 1585 cm^{-1} . After 10 months, the 80+RH and 80+RH+H+ samples show intense signal for the broad band of zinc carboxylate (POL-Zn) and extremely intense absorption for the crystalline zinc soaps (FA-Zn), with the split peak at $1537\text{--}1546\text{ cm}^{-1}$ displaying different ratios of relative intensity for the two samples. It is interesting to note that the mixtures prepared for this work, even after a short time, developed the type of peak splitting of the $\nu_{\text{as}}\text{COO}^-$ absorption in two main bands (centered at $1550/1530\text{ cm}^{-1}$) that has been observed by other researchers in older paints (Helwig et al. 2014; Osmond 2014, 2019). Though zinc oleate shows the $\nu_{\text{as}}\text{COO}^-$ bands at 1547 and 1527 cm^{-1} (Robinet and Corbeil 2003; Otero et al. 2014) and zinc azelate at 1556 and 1535 cm^{-1} , it's been suggested that in fact the doublet at 1550 and 1530 cm^{-1} may be related to a distortion of the symmetry around the zinc ion (Helwig et al. 2014). Further research on pure, synthetic compounds is needed to understand this aspect and completely exclude a convolution of bands of zinc palmitate with zinc azelate or oleate to explain peak splitting.

Tung oil showed less of a tendency to form FA-Zn, which were visible only as a shoulder (centered at around 1553 cm^{-1}) to the broad POL-Zn band, rather than as a distinct sharp peak, as observed with all other media, even after 10 months in hot and humid conditions (80+RH or 80+RH+H+) (Fig. 9.2).

Similarly, stand oil only developed a small amount of FA-Zn, as evident by a sharp peak at 1549 cm^{-1} , with a shoulder at 1532 cm^{-1} for the 80+RH+H+ sample after 21 days and the 80+RH and 80+RH+H+ after 10 months.

After 10 months the samples of Galkyd aged at RT and those that were briefly heated at $80\text{ }^\circ\text{C}$ show approximately the same level of POL-Zn formation and no FA-Zn. Similarly, the 80+RH and 80+RH+H+ samples display roughly equivalent high levels of POL-Zn, with the 80+RH+H+ sample showing slightly higher contribution of the sharp peak at 1550 cm^{-1} attributed to FA-Zn. Overall, these findings demonstrate that alkyd paints are to be considered at risk for the formation of FA-Zn and other zinc carboxylates in the same way as older oil paints, given that they may contain significant proportions of other bio-based oils (such as safflower oil in this case).

9.4 Conclusions

The results of this study advance our knowledge of the reactivity of zinc oxide with an expanded range of drying oils that are commonly encountered in many nineteenth- and twentieth-century paints and shed initial light on some of the parameters that may favor the formation of POL-Zn over FA-Zn.

The experiments and results described in this study showed that 4 days after mixing zinc oxide with various drying oils, no evidence of zinc carboxylate formation is detected with ATR-FTIR at RT. Heating at $80\text{ }^\circ\text{C}$ did not have a significant impact on the rate of formation of zinc soaps; however, the detrimental

effect of humidity combined with heat was confirmed, even after a short-term exposure of 48 h. It should be noted, though, that the transient exposure to artificial aging conditions took place at the early stages of cure.

Samples subjected to heat and humidity tended to quickly develop higher amounts of POL-Zn even after just 4 days. Over time (as demonstrated by the measurements taken after 10 months) the hydrolysis of the oil medium caused the formation of crystalline zinc soaps such as zinc stearate/palmitate (FA-Zn), at higher rates for the samples that were briefly exposed to hot and humid conditions. FA-Zn have been demonstrated to be potentially detrimental to paintings, given that the crystalline zinc soaps are found in protrusions and at the interface of paints that are delaminating.

Lowering the pH of the hot and humid air in some cases aggravated the process of POL-Zn and FA-Zn formation; in others the effect on zinc carboxylate formation was comparable to heat with high humidity without acidity, so further testing and longer-term study would be needed to fully understand the role of acidity in the formation of zinc soaps.

The viscosity (and initial cross-linking caused by pre-processing) of the oil was shown to matter more than the initial availability of free fatty acids (as indicated by the acid value) to the tendency of forming zinc carboxylates. Viscosity affects the mobility of the polymeric chains, thus slowing down the transport phenomena of metal ions and free fatty acids that have been demonstrated to be at the basis of the formation of detrimental FA-Zn. Obviously, other aspects such as degree of prepolymerization and chemical profiles of constituent fatty acids associated with specific oils also play a role, which should be elucidated further.

From a practical conservation standpoint, this study confirmed the important role of humidity with heat in the formation and evolution of zinc carboxylates. Thus, the impact of lining and consolidation (which may introduce heat and moisture) as well as aqueous cleaning procedures, whereby pH can be modified, should be carefully considered by conservators in their decision-making process, also in terms of the risk factors involving soap formation. Further studies should be conducted to confirm that the phenomena observed for exposures at early stages of cure are also replicable for older and fully cured paints.

Lastly, these qualitative experiments seemed to indicate that the type of industrial processing of the oil plays an important role in regard to soap formation. Of the three heat-processed oils evaluated (polymerized linseed, boiled linseed, and stand oil), the Winsor and Newton stand oil showed the lowest tendency to form both POL-Zn and FA-Zn. Considering that Ripolin paints were formulated with heat-bodied (stand) oils with addition of hard resins, these trends might provide some clues as to the stability of Ripolin paints and may indicate that, below a certain threshold, network-coordinated zinc soaps can, in fact, have a stabilizing effect on historical paints.

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