

# Oil Paints: The Chemistry of Drying Oils and the Potential for Solvent Disruption

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**ABSTRACT.** Oil paints have been used for hundreds of years in the European tradition of panel and canvas painting. Scores of different formulas have been used to find the correct paint with the desired properties. The alteration of the simple oil and pigment formula has led to elaborate systems with complex aging and solvent behavior. In the early stages of paint aging, the processes of autoxidation and hydrolysis dominate and determine overall structure, whereas hydrolysis determines long-term structural behavior. The ions and small molecules set loose by these processes further complicate the solvent behavior. Early hydrolysis of oils can lead to free fatty acids that can alter the initial chemistry and mechanical properties of paint films. The diffusion of small molecular weight compounds through the films of a painting may be quite extensive, with metal ions influencing drying rates and fatty acid anions (or neutral compounds) affecting stiffness or flexibility as well as forming accretions. Removal of these small compounds by solvents can result in loss of color saturation, as well as in embrittling the paint film by promoting cracking, thus affecting its overall strength and leading to an eventual collapse of the paint structure.

## INTRODUCTION

Oil paints have been used for hundreds of years in the European tradition of panel and canvas painting. Scores of different formulas have been used to find a paint with the desired properties. For example, it should dry quickly, but not too quickly; it should be flexible, but not too flexible; and it should not yellow. Attempts to maximize desirable properties in paints have led to considerable alteration from the basic formula of a simple oil and pigment mixture. Each alteration may have both an immediate consequence in the early behavior of the paint and a long-term one that may produce undesirable results.

Oils are esters of carboxylic acids, and for paints, drying oils are used, i.e., unsaturated acids with one, two, or three double bonds, e.g., oleic, linoleic, and linolenic acids. These acids are bound to a trihydroxy alcohol, glycerin, to form the corresponding esters. Two saturated fatty acids, palmitic and stearic acids, are also usually present in smaller amounts (Mills and White, 1987:26–40). Originally, the ability of paints to form dry films depended upon a formulation that, in general, had a larger amount of linolenic acid and, to some extent, linoleic acid. The unsaturated bonds, via an oxidation process, cross-link to form a tangled three-dimensional network. On the other hand, the ester bonds are important to the overall structural integrity of the dried oil film. However, these bonds may be easily hydrolyzed during and after the polymerization reaction, releasing free fatty acids. If hydrolysis of the ester bonds occurs before the film forms, the system becomes more acidic and may react with some of the pigments present in it. This paper analyzes

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in detail the possible effect of these reactions plus the influence of the presence of metal ions or the addition of solvents on the stability of the formulation over time.

### AUTOXIDATION PROCESS

Early scientific work examined oils by measuring weight changes in oil films as the oil dried. The drying of oils and oil paints is an autoxidation process where oxygen from the air is taken up and through a free radical process creates a three-dimensional network of bonds. Some of the oxidation products are small molecules that over time diffuse out of the oil film. Weight changes reflect the net change in weight produced by the uptake of oxygen and the loss of volatiles from the film. Net changes in weight can be considerable, up to a 14% increase or so in the first stages.

After an initial increase of weight due to oxygen take-up, the weight decreases. This reflects the loss of low molecular weight compounds that are diffusing out of the film. These have as yet not been identified. In oils with a lower content of linolenic acid than that of linseed oil, the weight loss may be greater than the

early original uptake of oxygen. The weight loss may produce voids or channels within the film affecting its behavior with solvents or even a collapse of the polymer structure. This weight loss from oil paint films predicts that over time the linseed oil-based paints will be less affected by diffusion of solvents than the poppy oil- or walnut oil-based paints because of a smaller loss of weight. Figure 1 plots the long-term weight loss in several oils over 1200 days. Note that the cold-pressed linseed oil loses far less weight than the other ones. Some of the oils are lighter in weight than when first applied, indicating severe degradation of the oil film polymer, which can continue for several years.

Figure 2 shows the weight changes in two red iron oxide paints prepared from cold-pressed linseed oil and a commercial (Kremer Pigments) linseed oil with lead, as litharge (PbO), added as a drier. There is still a measurable weight loss after 10 years, and although the loss remains small, it gives no indication of having stopped. This indicates that there is a loss of fatty acids or similar volatile compounds.

Figure 3 shows the weight changes in two alizarin-based oil paints, one in cold-pressed linseed oil and the other in linseed oil with litharge added as a drier. The long-term behavior is similar to the red iron oxide pigmented paints, i.e., the weight loss

FIGURE 1. The weight changes of pure oils after almost 1200 days of drying. CPLO = cold-pressed linseed oil.

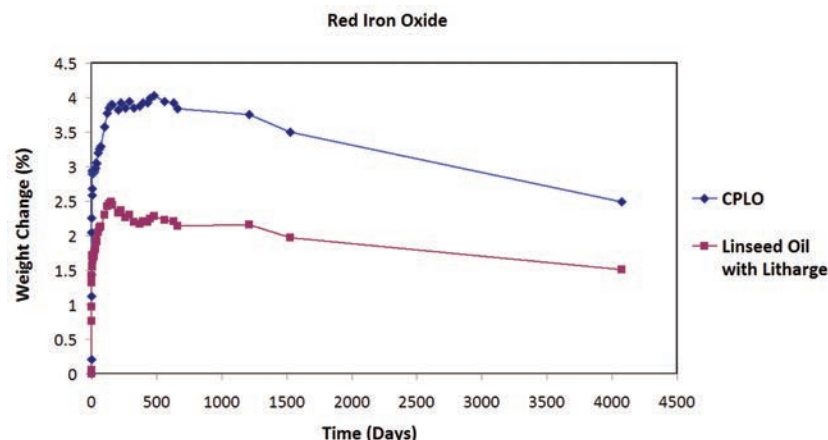
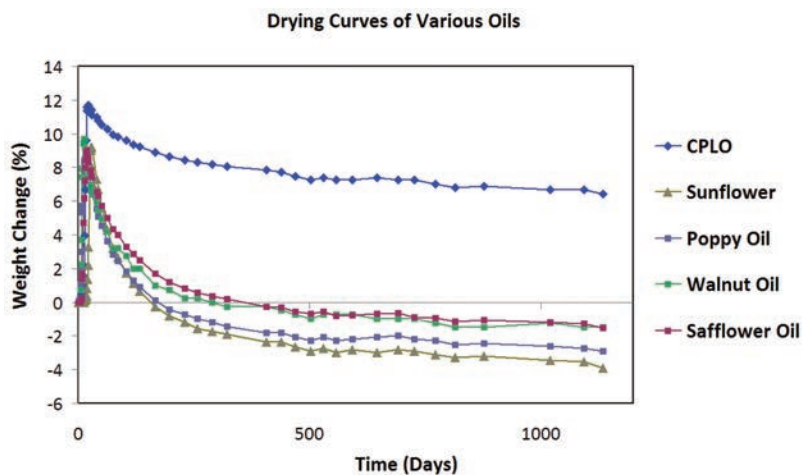


FIGURE 2. Weight changes for two red iron oxide paints over 10 years.

FIGURE 3. Weight changes for two alizarin paints similar to those in Figure 2.

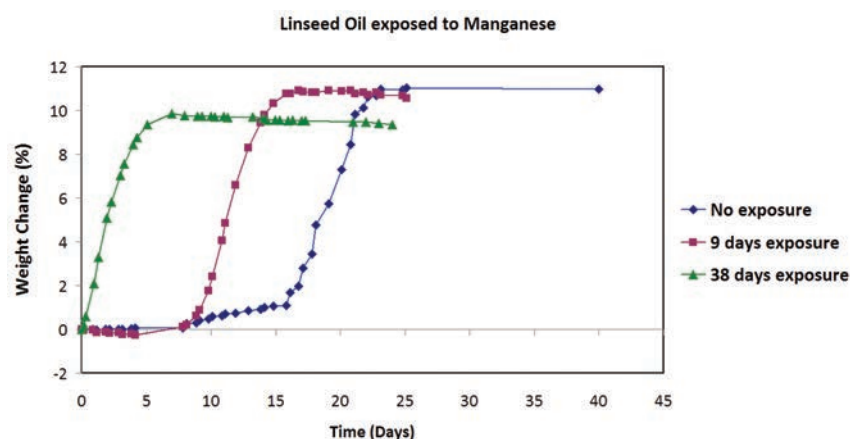
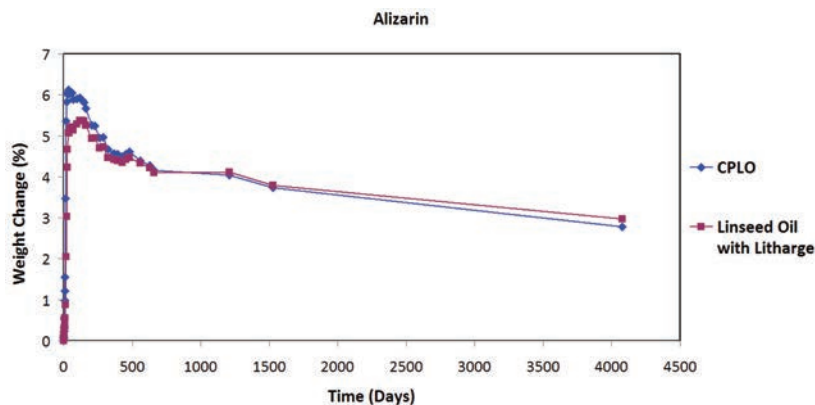


FIGURE 4. Changes in drying time of a cold-pressed linseed oil in contact with solid manganese dioxide for specified periods of time.

continues for years after the paint film has dried. However, both alizarin paints have similar weight changes, unlike the equivalent red iron oxide paints.

The initial autoxidation reaction can be induced to occur faster by the addition of certain metal ions, such as lead, manganese, and cobalt, generally called catalytic driers. They may be intentionally added or may be introduced as impurities or may be extracted from the pigment in the paint. Only a small amount of a catalytic drier, less than 0.5% by weight, is necessary for it to be effective. On the other hand, secondary driers, i.e., those that form complexes throughout the paint film, need to be present in larger amounts and typically account for over 10% by weight of the paint.

Figure 4 shows the changes in drying time of a cold-pressed linseed oil in contact with a small amount (15 mg) of solid manganese dioxide. Linseed oil, because of its increased acidity as hydrolysis progresses, is capable of partly dissolving the manganese dioxide. As contact time increases, more manganese ions will be dissolved and migrate into the oil. The manganese ions then accelerate the drying properties of the oil. This shows the influence of the acidity of the oil on its reaction with pigments and the ability of ions to diffuse into oils. A well-known example is the rapid drying behavior of oils mixed with a raw umber from Cyprus known to contain significant amounts of manganese dioxide. Drying oils may appear to be inert, but because of

autoxidation and hydrolysis they become reactive and are able to corrode metals such as copper over time.

Metal substrates, such as copper and lead, will also react with the oils' acidity and dissolve in sufficient amounts, influencing their drying time. Figure 5 plots differences in drying time of the same oil applied to metal surface. This shows again that diffusion of metal ions can influence drying.

Finally, slow-drying paints can be made to dry faster by applying them over a quicker-drying paint or an accelerating substrate. The behavior of a slow-drying alizarin paint in cold-pressed linseed oil applied over different substrates, ranging from an inert one to a copper plate and a lead paint, as well as with a catalytic drier, is shown in Figure 6.

The alizarin paint dries very quickly when placed on a copper substrate and slightly more quickly than cold-pressed linseed oil when placed on a previously dried lead white paint surface. The drying of the paint alone over an inert substrate and paint with a lead drier added is also shown for comparison. One of the puzzling results in this study was that the drying of alizarin paint over lead white was not accelerated as expected and reacted practically identically to that of the alizarin paint by itself. Furthermore, the paint in linseed oil with litharge had a delayed drying, and this could be related to the weight losses observed for these paints (see Figure 2).

FIGURE 5. Substrate effect on the drying behavior of cold-pressed linseed oil.

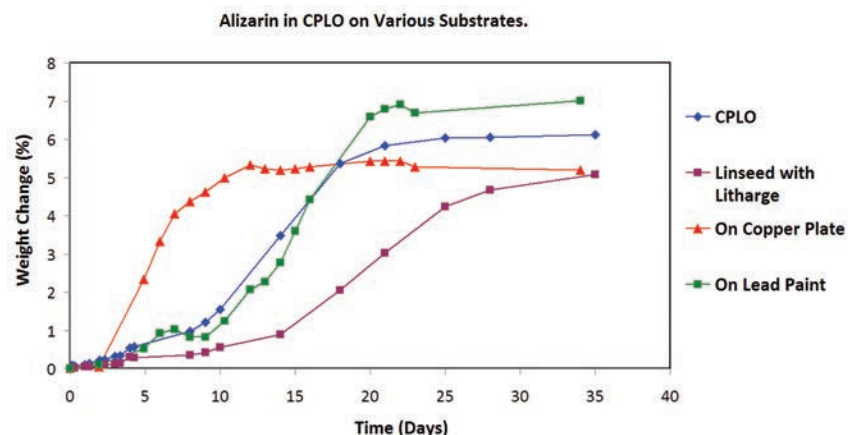
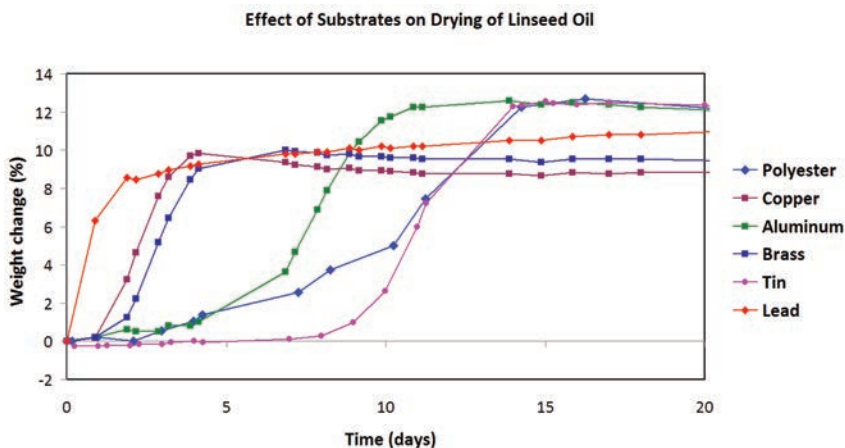


FIGURE 6. Drying behavior of a series of alizarin paints in cold-pressed linseed oil applied on: an inert surface, a copper metal plate, and a lead white paint. For comparison, the paint in linseed oil with a lead drier is also shown.

## HYDROLYSIS

In some paints hydrolysis occurs early, whereas after centuries, as for classical paintings, hydrolysis has been measured to have occurred to nearly 90% (Erhardt et al., 2001). The loss of almost three bonds per glycerin ester must have a significant effect on the structure of the oil paint. In order to investigate the effects of the total loss of ester bonds, paints were made with completely hydrolyzed oil and mixtures mimicking oil with 25%, 50% and 75% hydrolysis. These oils were mulled with various pigments to mimic old paints, that is, highly hydrolyzed ones.

The hydrolysis of drying oils frees fatty acids from their esters, and these acids can react with substrates or pigments. The autoxidation process can also produce small chain acids, and oxidation at the C9 position of the unsaturated acids can result in the formation of azelaic acid, found in the analysis of almost all oil paintings (Mills and White, 1987:26–40; van den Berg, 2002).

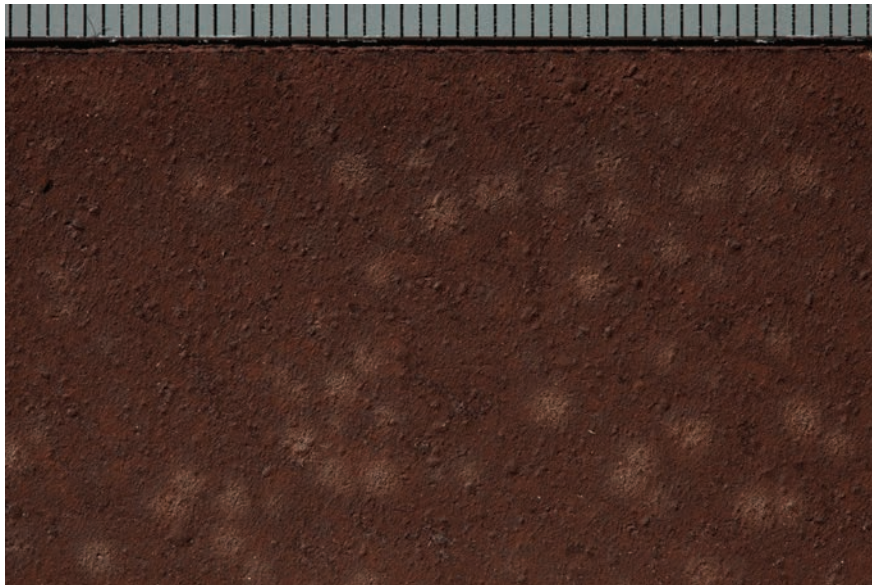
As a consequence of hydrolysis, large amounts of free fatty acids capable of migrating and/or reacting are created. Figure 7 shows a burnt umber paint that was prepared with partly hydrolyzed linseed oil and therefore has a high concentration of saturated fatty acids. Since these cannot cross-link, they are

segregated into nodules in the paint film after several months. Although this burnt umber film is an extreme case, partially hydrolyzed paint films may exhibit similar defects.

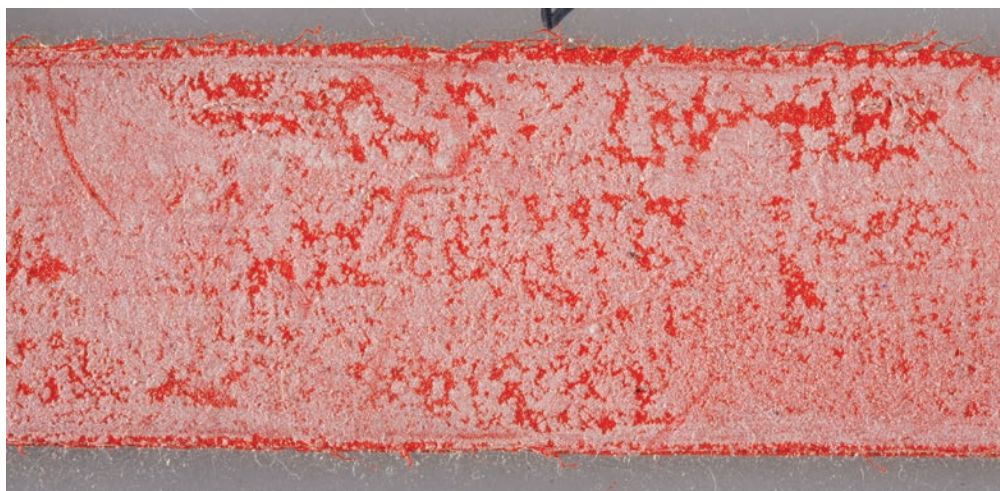
This phenomenon can also occur in commercial oil paints, as is shown in Figure 8. A 32-year-old commercially prepared cadmium red oil paint developed a significant white efflorescence on the surface over time as a result of the segregation of the free fatty acids that was therefore easily removed with organic solvents.

## METAL IONS

There is an initial time lag before oil paint films begin to take up oxygen, called the induction period. Since this may be rather long for some oils, attempts have been made to shorten it. As mentioned, certain metals, such as lead, cobalt, copper, and manganese, will decrease the drying time if dissolved in small quantities in the oil, as will certain pigments added to the paint. Another way of decreasing the drying time of an oil or paint is to apply it over a layer of paint that does dry quickly, particularly one containing the metal ions mentioned. Consequently, metal



**FIGURE 7.** Formation of nodules of free fatty acids in a burnt umber paint film after several months. Scale above is in millimeters.



**FIGURE 8.** Appearance of a 32-year-old commercial cadmium red oil paint. The paint strip is 20 mm wide. The surface is covered with a white efflorescence from the segregation of the free fatty acids.

ions were introduced into paints intentionally, such as by addition of driers, or unintentionally, by dissolution from added pigments or impurities. These can alter both the drying time and, eventually, the stability of the paint itself. Truly inert materials, that is, those that do not react significantly, will not add to the mechanical behavior of the paints. This can be demonstrated by preparing paints with very inert “pigments,” or, rather, fillers that do not significantly alter the properties of the oil film from that of an oil film alone.

The changes in the mechanical properties of paints can be illustrated by the stress-strain plots for different commercial burnt umber oil paints shown in Figure 9. These plots show that

increasing amounts of manganese ions lead to increased stiffness. Although small amounts of manganese may be good, larger amounts may not be necessarily better. The absence of manganese ions shows the catalytic effect of this ion in changing the long-term mechanical behavior of the paint.

The addition of inert materials to paint may not have any beneficial effects in itself, but inert materials have been and still are used as fillers to decrease the amount of expensive pigments used. To test their effect, silica, barium sulfate, and calcium carbonate were added to cold-pressed linseed oil. The resulting films, after several years, possessed as little strength as the pure linseed oil and were quite flexible. The ones that developed the least

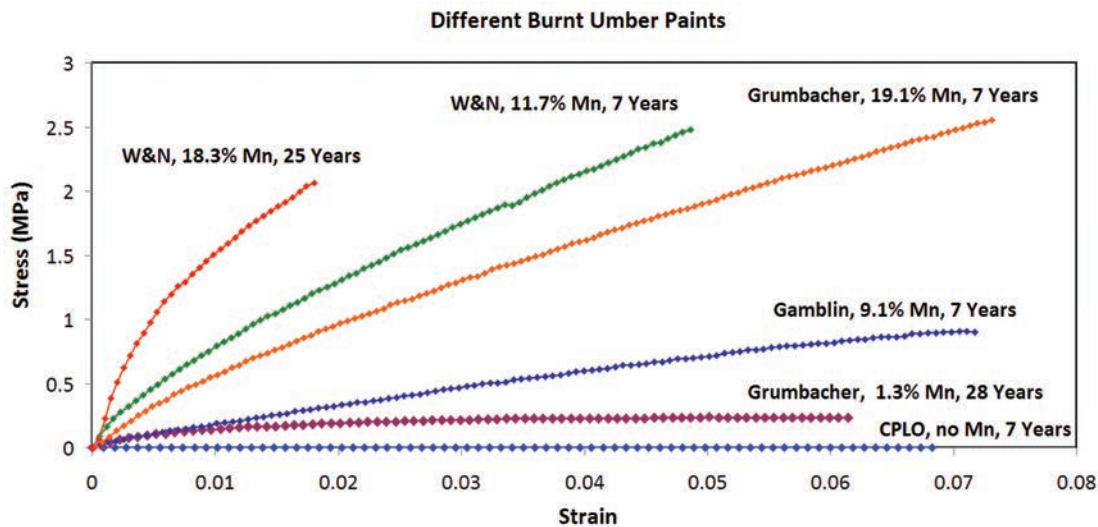


FIGURE 9. Stress-strain plots of commercial umber paints with varying amounts of manganese ions present. The plot for cold-pressed linseed oil without any manganese is added for comparison.

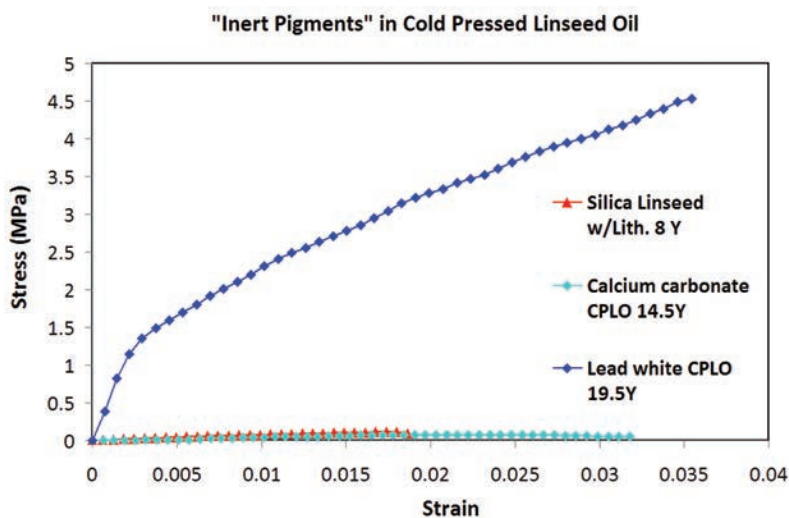


FIGURE 10. Stress-strain plots of “inert” pigments, silica and calcium carbonate in cold-pressed linseed oil. For comparison, the plot of CPLO with lead white is included. The data for the 8-year-old silica in linseed oil with litharge and the 14.5 year barium sulfate in CPLO plot along the abscissa as these films do not develop any mechanical properties.

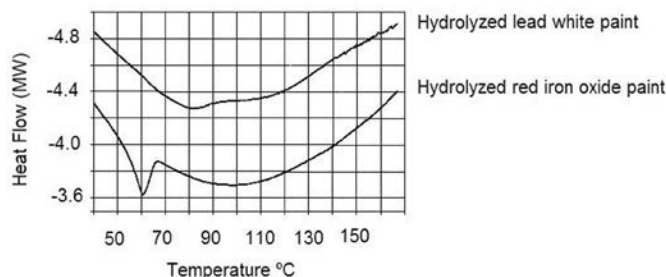
mechanical properties were the 14.5-year-old barium sulfate in a cold-pressed linseed oil film and the 8-year-old silica in linseed oil with litharge film, and therefore, they are not included in Figure 10, where the stress-strain data of the aged films are shown.

## SOLVENTS

The mechanical properties of a paint film depend upon its basic structure and the presence of small organic molecules that may act as plasticizers. The original structure of a paint film contains the ester bonds of the oil and the bonds produced by the cross-linking of the unsaturated fatty acids through autoxidation.

The loss of any of these bonds results in weakening the film strength. Any loss of the ester bonds must have a significant effect on the structure of the oil paint. After six years, the paints made with varying degrees of hydrolyzed oil appear as coherent films, but some disintegrate when solvents, such as acetone or toluene, are applied because these solvents can remove the low molecular weight compounds that contribute to the stability of the paints.

Solvents are not the only means of removing low molecular weight compounds. Heat can help evaporate saturated fatty acids, such as palmitic and stearic acids, and an improperly stored or displayed painting can become embrittled by the loss of these plasticizers. The long-term behavior of oil paints also seems to indicate that a small amount of evaporation of fatty acids



**FIGURE 11.** Differential scanning calorimetry plot of two paints made with 100% hydrolyzed linseed oil with lead white and red iron oxide pigments, respectively. The peak around 50°C for the red iron oxide paint reflects a phase transition of some fatty acid that does not appear in the lead white paint.

occurs over time. Improper temperature on a hot table may do so as well since the volatility of the fatty acids becomes significant above 70°C to 80°C (Erhardt et al., 2000).

Migration of fatty acids, for example, may occur from an area with little binding capability, such as one containing earth colors (iron oxide-based pigments), to an area where with considerable binding, such as one with lead compounds or zinc oxide. The graph shown in Figure 11 is a differential scanning calorimetry plot for two paints made from hydrolyzed linseed oil with lead white and red iron oxide pigments, respectively. Both paints form coherent films, but upon heating, a low melting phase transition in the red iron oxide paint occurs that is absent in the lead white paint. As indicated by the low-temperature phase transition at 50.5°C, this phase should be quite mobile and capable of migration. It is also apparent that lead-containing areas bind that mobile phase since this phase transition is absent in the lead white paint.

Table 1 shows the reactions of selected paints made with 100% hydrolyzed linseed oil and different pigments, such as red iron oxide, burnt umber, smalt, and raw umber. These paints mimic the worst case since all the ester bonds are hydrolyzed. The paints were immersed in the solvent for 5 minutes.

Acetone is the most aggressive solvent, to the point that the paints decompose after treatment. The toluene-treated paints were very embrittled and decomposed with the application of mechanical force. Water and hexane, both rather mild solvents, did not affect the paint films. Previously reported treatments of red iron oxide paints made with 25%, 50% and 75% hydrolyzed oil showed that the effects of hydrolysis became significant for paints with over 50% hydrolyzation (Tumosa et al., 2005).

The paint made with lead white and totally hydrolyzed linseed oil would be unaffected by the solvents based on the differential scanning calorimetry data obtained. The smalt was intermediate to the red iron oxide and white lead paints in behavior.

The loss of these low molecular weight compounds, regardless of whether this occurs by evaporation, migration within the paint, or removal by solvents, can embrittle a paint film and promote cracking as well as loss of color saturation (Tumosa et al., 1999; Erhardt et al., 2001).

## CONCLUSIONS

In conclusion, early hydrolysis of oils can lead to the formation of free fatty acids that can alter the initial chemistry and mechanical properties of oil paint films. The diffusion of small molecular weight compounds through the films of a painting may be quite extensive, with metal ions influencing drying rates and fatty acid anions (or neutral compounds) affecting stiffness or flexibility as well as forming accretions. Removal of these small compounds by solvents can embrittle a paint film and promote cracking. Loss of these small compounds by any mechanism will also result in a loss of color saturation. However, the nature of these compounds has yet to be determined.

This study has shown that there still are other questions that require answers. For example, the drying of alizarin paint is accelerated if the paint is applied on a copper substrate, but it is practically not influenced when the paint is applied over a lead white paint. Also, alizarin in a linseed oil with litharge showed an unexpectedly slow drying. Furthermore, the presence of inert materials decreases the mechanical properties of the paint films significantly.

**TABLE 1.** Reaction of paints made with 100% hydrolyzed linseed oil and different pigments after immersion with selected solvents for 5 minutes.

Pigment	Solvent			
	Acetone	Toluene	Hexane	Water
Red iron oxide	decomposed	embrittled	coherent	coherent
Burnt umber	decomposed	embrittled	coherent	coherent
Smalt	decomposed	embrittled	coherent	coherent
Raw umber	decomposed	embrittled	coherent	coherent

## REFERENCES

- Erhardt, D., R. Cunningham, and S. Rasanen. 2001. "Extraction of Material from Oil Paints by Solvents." In *Materials Issues in Art and Archaeology VI*, ed. P. B. Vandiver, M. Goodway, J. R. Druzik, and J. L. Mass, pp. 43–52. Boston: Materials Research Society.
- Erhardt, D., C. S. Tumosa, and M. F. Mecklenburg. 2000. Can Artists' Oil Paints Be Accelerated Aged? *Polymer Preprints* 41(2):1790–1791.
- Mills, J. S., and R. White. 1987. *The Organic Chemistry of Museum Objects*. London: Butterworths.
- Tumosa, C. S., D. Erhardt, M. F. Mecklenburg, and X. Su. 2005. "Linseed Oil Paint as Ionomer: Synthesis and Characterization." In *Materials Issues in Art and Archaeology VII*, ed. P. B. Vandiver, J. L. Mass, and A. Murray, pp. 25–31. Materials Research Society Symposia Proceedings 852. Boston: Materials Research Society.
- Tumosa, C. S., J. Millard, D. Erhardt, and M. F. Mecklenburg. 1999. "Effects of Solvents on the Physical Properties of Paint Films." In *Preprints 12th Triennial Meeting ICOM Lisbon*, ed. J. Bridgland, pp. 347–352. London: James & James.
- van den Berg, J. D. J. 2002. *Analytical Chemical Studies on Traditional Linseed Oil Paints*. pp. 9–52. Amsterdam: Molart (FOM).