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Long-Term Chemical and Physical Processes in Oil Paint Films

David Erhardt, Charles S. Tumosa and Marion F. Mecklenburg

Oil paints dry by polymerization. This 'drying' process may be substantially complete and the surface of the paint film dry to the touch within weeks, but measurable changes continue for years. Other, slower processes also continue, primarily hydrolysis of glyceride esters. This produces carboxylic acid groups as either free fatty acids (in the case of acid groups that have not reacted otherwise) or acid groups bound to the crosslinked oil matrix (in the case of acid groups that have engaged in polymerization reactions). These may react with pigments to form carboxylate salts (called soaps in the case of a fatty acid). These changes affect the physical properties of the paint and the way that conservation treatments affect it. This paper examines the extent of hydrolysis and soap formation in some naturally aged drying oil and paint films, the extractability of these materials in organic solvents, and measured and predicted changes over time in the physical properties of naturally aged paint films. Long-term physical and mechanical changes due to aging are minor compared to those produced by overcleaning or excessive exposure to heat.

INTRODUCTION

Plant oils are composed primarily of triglycerides, esters of glycerol and fatty acids. In drying oils, most of the fatty acids from which the triglycerides are derived are polyunsaturated. Drying oils, and oil paints compounded from them, dry by a process of autoxidation and subsequent polymerization of the unsaturated fatty acid groups in the triglycerides. This process is quite complex (see, e.g., the review by Wexler [1]). An oil paint film that is dry to the touch within weeks undergoes further reactions for decades longer. Chemically this includes further crosslinking reactions, oxidation of unsaturated acids and hydrolysis of glyceride bonds. Hydrolysis is a significant chemical reaction in a paint film even in the first few years [2]. Hydrolysis may yield saturated fatty acids (which lack the functional groups that react during the crosslinking process), unsaturated fatty acids that have not yet become part of the crosslinked oil matrix or otherwise reacted, acid groups attached to the matrix by bonds formed during polymerization, and short-chain

fatty or diacids formed by scission reactions of the unsaturated fatty acids. The acid groups produced by hydrolysis may react with metal ions from pigments to produce carboxylate salts (referred to as soaps in the case of a fatty acid). Free glycerol molecules are formed only after all three glyceride bonds are hydrolyzed, so that little free glycerol will be present unless extensive hydrolysis has occurred. The effects of hydrolysis cannot be understood unless the influence of other processes is also known. In this study the bulk mechanical properties of several paint films are followed and the extent of the hydrolysis and oxidation reactions examined.

Hydrolysis of oils

The reaction that produces the ester bonds in oils can be reversed. This process, called hydrolysis, yields the component fatty acids and glycerin. Partial hydrolysis, of one or two ester bonds, yields di- and monoglycerides, respectively. If any of the fatty acids have reacted to become part of the polymer matrix, hydrolysis yields an acid group attached to the polymeric matrix by the bond formed during polymerization. That hydrolysis of

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glycerides occurs has been well known for a long time. The hydrolysis of oils (and fats) with alkali to produce soaps (the fatty acid salts of the alkali) was probably one of the first chemical reactions discovered. The pioneering chemist Carl Wilhelm Scheele first isolated glycerin in the late 1700s (he also discovered oxygen, nitrogen, chlorine, and other elements and compounds). Scheele showed that glycerin and fatty acids could be produced by the action of lead oxide on fixed (vegetable) oils in the presence of water [3] (it was not until more than a hundred years later that the term hydrolysis was used to describe the reaction). It was realized very early in the last century that hydrolysis of oil was responsible for many of the changes (some good, some bad) in the properties of paints stored for long periods of time (years), that the presence of water promoted hydrolysis and soap formation [4], and that completely ionomeric paints could be prepared directly from soaps of hydrolyzed drying oils [5]. O'Neill and Brett, in examining the reactions taking place in paint films, looked at the amount of material that could be extracted from oil paint films after aging, and the amount of metal ion in the extracted material. They concluded that paint films reacted fastest with basic oxide pigments, more slowly with carbonate pigments, and even more slowly, if at all, with inert oxide pigments. They also concluded that the formation of metal soaps contributes to the particular properties of white lead and zinc white oil paints [2].

Hydrolysis of dried oil paint films

While some hydrolysis and soap formation with free fatty acids present in drying oils occurs very quickly, extensive hydrolysis of paint films occurs over a time-span longer than is of concern industrially. Most oil paint research focused on changes that occur in paints before application or during the drying process after application. Hydrolysis in unpolymerized oil was of great concern because it affects the mixing, storage and working properties of the paint. Research on the behaviour of paint after application, though, focused on the oxidative polymerization process, since hydrolysis and soap formation in the dried oil were much slower. Consequently, few reports examined the process until Boon and co-workers reintroduced the concept and showed that hydrolysis could be quite extensive over the museum time-scale [6, 7]. Using a derivatization method that distinguished between esterified and non-esterified carboxylic acid groups (but not between free acids and ionic, or soap, moieties), they showed that the degree of hydrolysis increased with age, and concluded that the

extent of hydrolysis was more than 90% in some older paint samples. However, they also made a number of unsubstantiated statements regarding other aspects of aging, especially regarding the physical and mechanical aspects of aging. It is unlikely that the evaporation of glycerol, which has a boiling point of 290°C (with decomposition), would be a significant process at normal temperatures, especially from within a solid matrix such as the polymerized oil. In fact, their results show that significant amounts of glycerol are present in quite old paints. Work by the present authors showed that the relative amounts of glycerol increased with increasing hydrolysis, primarily due to the fact that all three glycerol ester bonds must undergo hydrolysis to yield free glycerol [8]. Boon *et al.* also inferred from their data that the paints are mostly in an ionomeric form without presenting data showing the relative amounts of free acid versus carboxylate present. They cite studies showing that old paintings may have little extractable material as supporting their statement that the free acids are present as soaps; however, the study cited was of previously cleaned (i.e., solvent treated) paintings that likely had little easily extractable material left. Work by the present authors shows that many, if not most, of the free fatty acid molecules are present as the acids rather than as soaps [8]. Boon *et al.* also mention repeatedly that conversion to the ionomeric form is responsible for the paint film becoming hard and brittle, although this association has not been demonstrated in their or any other study. To the contrary, previous work by the present authors, summarized in this article, shows that the strength and stiffness of paint films change in a way that can be modeled mathematically, and changes over long periods of aging can be predicted. The rate of changes in these properties slows considerably as the paints age, and a paint film hundreds of years old should not be much stiffer or more brittle than a paint film only decades old. If a paint is going to become brittle, as for instance zinc oxide pigmented paints do, it does so quite early. It is easily shown, though, that paint films do become brittle after prolonged exposure to high temperatures or solvents [9, 10]. The present authors have in fact prepared a number of completely hydrolyzed paint films from mixtures of pigments and free fatty acids (derived from the hydrolysis of drying oils). These films, which are now several years old, are coherent and some are as flexible as comparable paints prepared from the original oils. This is despite the fact that glycerol, which would act as a plasticizer, was removed during the hydrolysis of the oils and is not present. Studies of these paints will be reported later.

SAMPLES AND EQUIPMENT

Paint samples consisted of films of pigment and linseed oil (cold-pressed unless otherwise specified) with no other additives. They were naturally aged in the laboratory at 40–50% RH and 22°C under ambient light. Paint films were cast on polyester sheets, and were removed as needed. Oil specimens were the same cold-pressed oil from which the paint samples were prepared. Paint specimens were also removed from fragments of panel paintings at least 200 years old. These fragments are from French panel paintings dating from the eighteenth century that had previously been donated for research purposes. Specimens were weighed on a Mettler balance, model AT201, to within 0.01 mg. Extractions were performed in 50 mL of reagent-grade solvents for 24 hours. Stress-strain measurements were made on screw-driven tensile testers, the samples being approximately $0.2 \times 6 \times 125$ mm. The procedure has been described previously [11]. Fatty acid composition was determined and quantified by gas-chromatography as previously described [8].

The percentages of free, ionized (soap), and esterified fatty acids were determined as follows. Free acids were removed from a small paint sample by extraction with a large excess of dichloromethane, accompanied by grinding of the sample with a glass rod to ensure complete extraction. The solid residue was separated and rinsed with more solvent, which was also separated and combined with the first extract. This combined extract contains the free fatty acids. Several milliliters of diethyl ether were then added to the solid residue. A drop of dilute (1 N) hydrochloric acid was added to convert any soaps to free acids, which are extracted (with agitation) into the ether, which is removed. The acidified sample is extracted with two more aliquots of ether, and the ether extracts are combined. This step is conducted quickly to minimize any hydrolysis of the esterified acids. The water is evaporated from the solid residue, and the remaining esterified acid groups are removed from the residue by standard procedures, i.e., hydrolysis with KOH in methanol, acidification, and extraction with ether. The three extracts (free, soap, and ester acids) are evaporated. A known amount of tetratriacontane (the 34-carbon straight-chain alkane) in hexane is added to each of the three extracts as an internal standard. The samples are trimethylsilylated with *N,O-bis(trimethylsilyl)trifluoroacetamide* (BSTFA) and analyzed by gas-chromatography as previously described [8]. The ratios of the areas of fatty acid peaks to the areas of the tetratriacontane peaks are used to calculate the

relative amounts of fatty acids present as free acid, soap, and ester. Small amounts of glycerides were observed in the chromatograms of the extracts of the unhydrolyzed samples; however, these were small enough not to affect the calculations and were not taken into account.

RESULTS AND DISCUSSION

Hydrolysis

Hydrolysis within two years was measured to be as extensive as 20% in specimens of pure cold-pressed linseed oil or in the same pigmented oil stored under conditions of 40–50% RH and 22°C, within the environmental range typically recommended for museums. Analysis of oil paint films from unprovenanced European panel paintings at least 200 years old indicates that the extent of hydrolysis approaches 80% in some cases. Hydrolysis is a process that can be detected early in the drying of paint films. Increases in the amounts of free saturated fatty acids (palmitic and stearic) can be detected within a year. These acids are not involved in any oxidative process (e.g., crosslinking) and although they generally account for less than 10% of the total fatty acid composition of linseed oil, they are preferentially located in triglyceride positions 1 and 3 and are more easily hydrolyzed than acids located at the 2-position [12]. Therefore, their hydrolysis rate represents an upper limit on the total hydrolysis rate of the polymerized glyceride units. Azelaic acid is formed by oxidative scission at the C9 double bond in the 18-carbon unsaturated acids (oleic, linoleic, and linolenic). Figure 1 plots the total amount of azelaic acid in a cold-pressed linseed

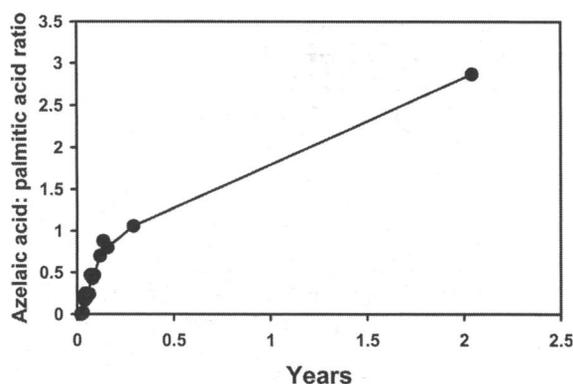


Figure 1 Proportion of azelaic acid in a cold-pressed linseed oil film over time, expressed as the ratio of the amount of azelaic acid to the (constant) amount of palmitic acid.

oil film as a function of time. The amount of azelaic acid is plotted as the ratio of the amount of azelaic to that of palmitic acid (which remains constant, since palmitic acid does not react). If azelaic acid is formed from unsaturated fatty acids bound by glyceride ester bonds, the resulting azelate group is also attached to the glyceride or polymerized oil matrix, and hydrolysis must occur before the azelate is present as the free acid. Two separate reaction processes (oxidation at the C9-position of unsaturated acid groups and hydrolysis of the ester bond) must occur before free azelaic acid is formed, so the rate of formation of free azelaic acid will be lower than the rate of the hydrolysis step. Hydrolysis of azelaic acid precursors can occur before the oxidation step, but the free azelaic acid produced by this reaction sequence will only be seen after subsequent oxidation. Thus the rate of formation of free azelaic acid (relative to the final total amount of azelaic acid produced) is a lower limit of the rate of the one reaction, hydrolysis of unsaturated fatty acids that oxidize to azelaic acid. Unsaturated acids (or their polymerized forms) fill the less easily hydrolyzed 2-position in glycerol preferentially to the saturated acids, and the rate of hydrolysis of their glyceride ester linkages should be slower than that of the saturated fatty acids, but faster than that of the appearance of hydrolyzed azelate. The measurement of hydrolyzed acids (palmitic, stearic, azelaic) is complicated by a common process. Free fatty acids will react with many pigments to form soaps. Soap formation ties up any free acid and prevents it from being easily extracted by solvents or lost by thermal evaporative processes. Free azelaic acid, with two acid groups, should be approximately twice as likely to be present as a salt. By carefully selecting solvents and by mild acid treatment the relative proportions of fatty acids present as glycerides, free acids, and soaps can be determined. Figure 2 shows how the amounts of azelaic and palmitic acids present as free acid and as soap increase over time in a lead white paint film. The total fraction of hydrolyzed acid (free plus soap) is also shown. It can be seen that for palmitic acid, the amount present as the free acid is about twice that present as the soap. As expected, the fraction of hydrolyzed azelaic acid is less than that of palmitic acid, and a greater percentage of the hydrolyzed difunctional azelaic acid (about half) is present as a soap. (An azelate 'soap' may have one or both carboxylic acid groups converted to the carboxylate salt; the experimental method does not distinguish between the two possibilities.) Data for stearic acid were also determined and are nearly identical to those for palmitic acid, but are omitted for clarity.

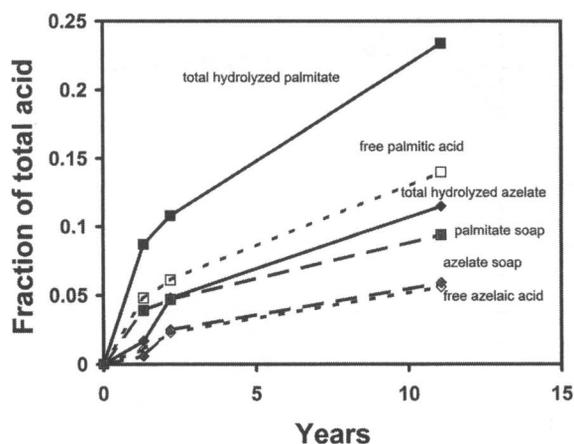


Figure 2 Proportions of azelaic and palmitic acids present as free acid, soap, and total hydrolyzed (free plus soap) in a lead white in cold-pressed linseed oil paint film as a function of drying time. The amounts are expressed as fractions of the total acid present in the paint (free plus soap plus acid bonded by glyceride esters).

Oxidation

The autoxidation process of paint films can be monitored by measuring the initial weight and weight changes over time (so-called Weger curves [13–15]) as well as by determining the amount of azelaic acid formed. Azelaic acid may be formed by oxidative scission of the double bond at the C9-position of the unsaturated fatty acids and is initially bound to glyceride (or the cross-linked matrix) by the original glyceride ester linkage. On hydrolysis it becomes a free acid and may bind to metal ions in the pigment. In pure linseed oil, azelate formation was found to have an incubation period of 5–10 days. The amount increased rapidly for about two months, and then more slowly for the next two years. This parallels nicely the measured weight gains of the bulk paint films. Figure 3 shows a typical weight gain curve for lead white in cold-pressed linseed oil, which can be compared with the rate of formation of azelaic acid shown in Figure 1. After an incubation period of several days, the paint gains weight rapidly for about two weeks, and more slowly for several months. Longer aging results in a slow weight loss. It is clear from the initial rapid weight gains that uptake of and reaction with oxygen are primarily responsible for the initial shape of the Weger curve. However, once most of the sites that are readily oxidized have reacted, the contribution of other, concurrent processes such as the loss of volatile compounds can be seen as a gradual loss of weight. These low molecular weight compounds may

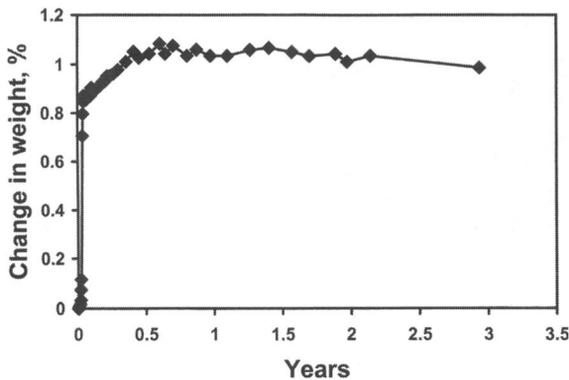


Figure 3 Change in weight of a lead white in cold-pressed linseed oil paint film as a function of drying time.

be present in the original oil, formed as byproducts during the initial oxidative polymerization, or later as the paint film slowly oxidizes over time.

Polymerization and crosslinking

In the early stages of drying, polymerization and crosslinking can be inferred from the decrease in the amount of extractable low molecular weight polymers as the film ages. This is easily determined through solvent extraction studies. Figure 4 shows the changes in the amount of extractable material over the first several years for a paint prepared from lead white pigment and cold-pressed linseed oil, and a commercial paint containing titanium white in alkali-refined linseed oil. The major

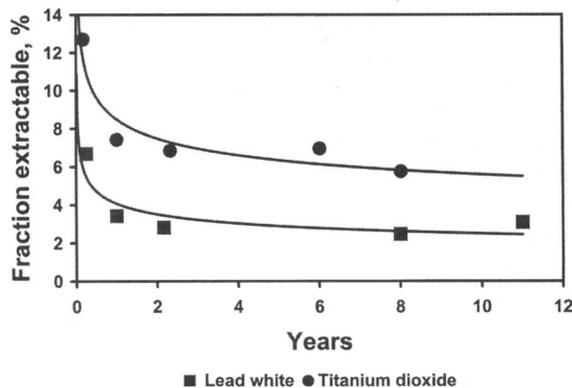


Figure 4 Total of extractable material in a paint prepared from lead white pigment and cold-pressed linseed oil, and a commercial paint containing titanium white in alkali-refined linseed oil, as a function of drying time. The values are the extractable fraction of the total paint, and are not corrected for pigment weight.

changes occur within two years, with slower changes continuing over the next 10 years. Since the weight of the paints is either increasing or stable during this time, the reduction in the amount of extractable material (mobile phase) must be due to the incorporation of some of this material into the polymer matrix (through continued crosslinking), or the conversion of free fatty acids to insoluble metal salts, rather than a loss of volatile material.

Mechanical properties

Fully hydrolyzed paint films can be produced relatively quickly by heating at both high RH and high temperature. Paint samples heated under conditions ranging from 75 to 100% RH and 80 to 100°C hydrolyze completely and become brittle and easily fractured. The brittleness of these samples, however, is due to the loss of low molecular weight plasticizers rather than changes brought about by conversion to a theoretical ionomeric composition. A fully hydrolyzed paint film can be created through synthetic means starting with a hydrolyzed linseed oil, grinding in pigment, and casting the resulting mixture as a film. Such paint films have been prepared, and some are more flexible than the equivalent paint prepared from unhydrolyzed oil. This is true even though they contain no glycerol ester bonds and are potentially totally ionomeric. More complete results will be reported elsewhere. Thus, hydrolysis of a paint film over time will not necessarily cause a paint film to become brittle. A paint film will become stiffer and more brittle, however, if it is heated (at any relative humidity) or treated with solvent. Both procedures remove low molecular weight material, by evaporation and extraction, respectively. It was shown previously that evaporation of these plasticizing components does not occur to any significant extent at normal temperatures [10]. Thus, a properly prepared paint film should remain flexible unless it is mistreated by overexposure to heat or solvents and loses low molecular weight plasticizing compounds. This statement is supported by Figure 5, which shows stress-strain curves measured for paint films of lead white in cold-pressed linseed oil one and 10 years old, as well as later curves extrapolated from these and other measured curves. The mathematics of the extrapolation are described by Mecklenburg and Tumosa [16]. Briefly, it was found that plots of stress at a specific strain versus \ln time were linear for each paint, and could be extrapolated to predict stress at that strain for films of any age. Breaking strain could be predicted similarly by plotting breaking strain versus time. By

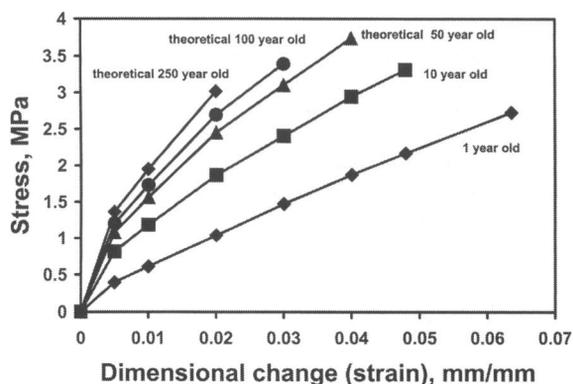


Figure 5 Stress-strain curves measured for paint films of lead white in cold-pressed linseed oil one and 10 years old, and later curves extrapolated from these and other measured curves. From Mecklenburg and Tumosa [16].

calculating stresses at various strains (as well as breaking strain) for a film of a specific age, a stress-strain curve can be constructed. These are shown as the theoretical curves in Figure 5. It can be seen that the properties change very slowly after about 50 years, and that even a 250-year-old paint film will not be substantially stiffer or more brittle than a film only decades old. It is significant that the 10-year-old lead white film is already almost 25% hydrolyzed, and almost half of the freed fatty acids have been converted to salts (see Figure 2). In a study of ethylene-acrylic acid copolymers, Bonotto and Bonner found that effects on physical properties such as stiffness and strength were readily apparent by 10% conversion to ionomer (salt form), and peaked at about 30% conversion [17]. While the system they used is not identical to a dried oil, it seems that if hydrolysis and soap formation were to have significant effects on mechanical properties, they would be apparent in the 10-year-old sample. That only minor changes are seen supports the extrapolation showing that much older films, with a higher extent of hydrolysis and degree of soap formation, will still be relatively flexible.

CONCLUSIONS

The existence of long-term processes in oil paints is readily demonstrated by some simple experiments. Plots of weight over time show that the process of weight gain is quite slow after two years, but if the data were extrapolated the theoretical maximum weight gain (derived from the weight gain of pure linseed oil and correcting for the weight of pigment present) would not

be reached for hundreds of years, if at all. Hydrolysis of the glyceride ester bonds is a slow process relative to the initial polymerization reactions, and even samples hundreds of years old may have substantial portions of the glyceride ester bonds intact. Plotting data for the changes in mechanical behaviour also shows that the major changes occur within years or decades, but also predicts that measurable changes occur for well over 50 years and approach a limiting value after about 150 years.

The major processes in oil paints can be grouped into polymerization, hydrolysis, oxidation, and soap formation (if a pigment capable of reacting to form soaps is present), along with accompanying changes in the mechanical properties. Within the first few years the amounts of extractable materials decline as the smaller molecules continue to crosslink. In addition, the amount of soluble (free) fatty acids increases due to hydrolysis of the triglycerides. A portion of this may react with metal ions present in many pigments to form insoluble metal soaps. Hydrolysis reduces the number of crosslinks between the glycerides. However, other crosslinking reactions must occur since the total amount of extractable material decreases over time. Since the free fatty acids tend to keep the paint film flexible, any stiffening of the paint film must come from further non-ester crosslinking and/or possibly from soap formation as well. One possibility is that crosslinks occur through multivalent metal ions. Azelaic acid groups still bound to the glyceride by the original glyceride ester bond can form salts through the free acid group formed by oxidation. A multivalent metal that formed a salt with more than one such acid group could function as a crosslink, and possibly increase the stiffness of the paint. However, in a study of synthetic polymers containing acrylic acid groups, it was found that multivalent metal ions had no more effect on physical properties than the equivalent amount of monovalent ions, and that the change in physical properties was solely a function of percent conversion to ionomer, and not of the type or valency of the metal ion [17]. Whatever the case, these processes do not have a major effect on the mechanical properties, since tests of untreated paint films kept under moderate environmental conditions show that changes in the mechanical properties have already slowed significantly within the first few decades.

The implications for conservation follow, in part, from previously reported work on calculating ranges of relative humidity appropriate for the museum environment [18, 19]. If paints retain a reasonable elastic region (the amount they can be deformed without permanent change) throughout their lifetime, then the allowable

RH fluctuations calculated using data from the available paint samples up to 20 years old will apply to paint throughout its normal aging process. The amount of dimensional change that will occur in unrestrained glue or gesso (the materials in canvas paintings most responsive to RH changes) or tangential wood (the material in panel paintings most responsive to RH changes) in a range of $\pm 15\%$ RH about a median of 50% RH is about 0.004, or 0.4%. It can be seen from Figure 5 that even 250-year-old paint is predicted to require about four times this much distortion before it breaks, while the elastic limit is similar to newer paints (about 0.4%), and would not be exceeded by such RH fluctuations even assuming worst case conditions (attachment of the relatively RH-unresponsive paint to a highly responsive substrate that is exposed to the RH extremes long enough to respond fully). It was shown previously that oil paint films retain their elastic properties even after extreme solvent treatment (24-hour immersion). While the loss of part or all of the plastic region upon aging, heating or solvent treatment does have implications for handling and transport (a paint film would be more likely to break rather than permanently distort if mistreated), it does not affect the choice of appropriate environmental conditions.

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Résumé — *Séchage de peintures à l'huile par polymérisation. Ce processus de « séchage » peut être pratiquement complet, et la surface du film peint paraître sèche au toucher durant des semaines, mais des changements notables continuent de se produire pendant des années. Par ailleurs, un processus plus lent continue de se développer, en premier lieu l'hydrolyse des esters glycérides. Ceci produit des groupements d'acides carboxyliques tels que des acides gras (dans le cas de groupements acides qui n'ont pas réagi par ailleurs), ou encore des groupements acides pontés avec la matrice huile (dans le cas de groupements acides impliqués dans des réactions de polymérisation). Ceux-ci peuvent réagir avec les pigments pour former des sels carboxyliques (appelés « savons » dans le cas des acides gras). Ces changements affectent les propriétés physiques de la peinture et la façon dont les traitements de conservation la modifient. Cet article examine l'extension de l'hydrolyse et la formation de savon dans quelques huiles siccatives vieilles naturellement et des films de peinture, l'extractibilité de ces matériaux dans des solvants organiques, et les changements prévus et mesurés dans le temps des propriétés physiques de films de peintures vieilles naturellement. Les changements physiques et mécaniques à long terme dues au vieillissement sont minimes en comparaison de ceux produits par un nettoyage généralisé ou une exposition à la chaleur.*

Zusammenfassung — *Ölhaltige Malschichten trockenen durch Polymerisation. Dieser "Trocknungsprozess" mag binnen Wochen im Wesentlichen angeschlossen sein und die Oberfläche trocken erscheinen, doch messbare Veränderungen treten noch Jahre danach auf. Auch andere, langsamere Prozesse schreiten fort, vor allem die Hydrolyse der Glyceridester. Dabei entstehen Carboxylgruppen, entweder als freie Fettsäuren (in dem Fall, daß die Säuregruppe nicht anderweitig reagiert hat) oder als Säuregruppen, die an die vernetzte Ölmatrix gebunden sind. Diese können mit Pigmenten zu Carboxylaten reagieren (Salze, die im Fall der freien Fettsäuren Seifen genannt werden). Bei diesen Prozessen werden die physikalischen Eigenschaften verändert, aber auch die Art und Weise wie sie auf Restaurierungsmaßnahmen reagieren. In dieser Arbeit wird das Ausmaß der Hydrolyse und der Bildung von Seifen an einigen natürlich gealterten Ölfilmen und Malschichten untersucht sowie die Extrahierbarkeit der entstehenden Materialien durch organische Lösungsmittel. Außerdem werden die erwarteten und die gemessenen Änderungen der physikalischen Eigenschaften miteinander verglichen. Dabei sind die Änderungen der mechanischen und physikalischen Eigenschaften gering im Vergleich zu denen, die durch übermäßiges Reinigen oder den Einfluß von Hitze verursacht werden.*

Resumen — *Las pinturas al óleo secan por polimerización. Este proceso de 'secado' puede llegar a completarse en gran medida, considerándose seca la superficie al tacto en semanas, aunque los cambios sustanciales continúan durante años. Otros procesos más lentos también continúan, principalmente la hidrólisis de los ésteres glicéridos. Esto produce tanto grupos ácido carboxílicos como ácidos grasos libres (en el caso de grupos ácidos que no han reaccionado anteriormente) y grupos ácido unidos a la matriz oleosa entrecruzada (en el caso de grupos ácido que se han incluido en relaciones de polimerización). Estos pueden reaccionar con pigmentos para formar sales carboxiladas (llamadas jabones en el caso de ácidos grasos). Estos cambios afectan las propiedades físicas de las pinturas y la manera en la que los tratamientos de conservación pueden afectarlas. Este artículo examina el grado de hidrólisis y de formación de jabones en películas de aceite secativo y de pinturas al óleo envejecidas naturalmente; también se considera la capacidad de extracción de estos materiales en disolventes orgánicos y los cambios en el tiempo que pueden ser previstos en las propiedades físicas y mecánicas, causadas principalmente por el envejecimiento de las películas de pintura envejecidas naturalmente. Los cambios físicos y mecánicos a largo plazo debidos al envejecimiento son menores comparados con aquellos producidos por limpiezas excesivas o por sobreexposición al calor.*