

NATURAL AND ACCELERATED THERMAL AGING OF OIL PAINT FILMS

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

ABSTRACT

Processes that occur in oil paints after the initial drying stage include the hydrolysis of glyceride ester linkages, the formation of soaps, and the volatilization of low molecular weight compounds. The nature, amounts and distribution of the soluble components of paint films serve as indicators of the relative rates and extent of these processes. Comparisons of naturally aged paint with paint aged at an elevated temperature (80°C) indicate that thermal aging distorts the relative rates of these processes and does not accurately simulate the natural aging of oil paint. The relevance to conservation research of thermally aged paint, especially samples aged above the melting point of paint components, is questionable.

INTRODUCTION

Drying oils used in artists' paints serve as the (more or less) transparent binding medium in which the pigment is contained. During drying, the oil polymerizes to form a tough, rubbery matrix. Surface oxidation, hydrolysis, and evaporation of low molecular weight components all contribute to the changes that occur in the dried oil matrix subsequent to the initial drying process. In addition, the removal of extractable material during exposure to solvents tends to embrittle and stiffen the paint layer and desaturate the colour.

COMPOSITION OF DRYING OILS

Oils as extracted from their vegetable sources are formed by the chemical combination of glycerin (glycerol) and fatty acids. Glycerin has three alcohol groups, each of which can combine with a fatty acid to form an ester. Combining glycerin with one fatty acid yields a monoglyceride, with two fatty acids, a diglyceride, and with three, a triglyceride. Oils consist primarily of triglycerides, with smaller quantities of mono- and diglycerides and free, uncombined fatty acids and glycerin. Fatty acids are of two basic types. Saturated fatty acids have no double bonds in the hydrocarbon chain and are relatively chemically stable. Unsaturated fatty acids have one or more reactive double bonds in the hydrocarbon chain. These double bonds can engage in a number of reactions, including oxidation to form smaller compounds or crosslinking to form larger ones. Glycerides formed from unsaturated fatty acids are similarly reactive. Triglycerides in drying oils are formed primarily from unsaturated fatty acids.

DRYING OF OIL PAINTS

The 'drying' process of an oil paint begins rapidly once it is spread out as a thin film and exposed to air and light. During the drying process, the reactive unsaturated fatty acid components either polymerize and attach to unsaturated acids in other glyceride molecules to form crosslinks, or degrade to smaller compounds, primarily di-acids. Polymerization occurs primarily through oxidative processes. The crosslinked triglyceride matrix is the primary component of a dried oil. When the chemical process of drying is complete, the polyunsaturated fatty acids are no longer present either as free acids or as esters in glycerides (small amounts of the less reactive mono-unsaturated oleic acid often remain). Most of the material is bound up in the polymer matrix. The original compounds that remain soluble in a dried oil are the small amounts of glycerin, and compounds derived from only unreactive saturated fatty acids, including free saturated fatty acids, and the mono-, di- and triglycerides that originally contained only saturated fatty acids. Soluble material also includes the degradation products, but not the polymers, of the unsaturated acids.

Heating drying oils in the absence of oxygen during processing can induce partial prepolymerization by direct, non-oxidative, condensation reactions. Once applied, these partially prepolymerized oils finish drying through oxidative mechanisms like those of unheated oils.

Paint films are sometimes heated after becoming dry to the touch, but such heating is relatively gentle and probably involves completion of the oxidative crosslinking already under way rather than true thermal polymerization. Subsequent heating, after the paint has dried and no more unsaturated fatty acid components are present, results in other changes, as discussed below.

AGING OF OIL PAINTS

Initial 'drying' process

Oil paints become dry to the touch quite rapidly, skinning over and forming a rubbery film within days or weeks. The reactions that lead to this drying are far from over, however. The chemical processes of drying continue, and significant amounts of unsaturated fatty acids and reactive intermediates can be detected for months. The chemical drying process can be considered complete when all of the reactive unsaturated compounds and intermediates are gone, usually within several years. At this point, much slower processes take over.

Oxidation

Oxidation of dry oil paints seems to be primarily a surface phenomenon. Analyses of bulk samples of older paints do not differ substantially from those for new ones in terms of the proportion of oxidative decomposition products. For example, the amount of azelaic acid does not increase substantially once the drying process is complete. Oxidation can be induced by light exposure, and many of the resulting fragmented compounds are volatile enough to be lost by evaporation [1, 2].

Hydrolysis

Glyceride ester linkages can hydrolyse to yield the component compounds. Hydrolysis of triglycerides will yield, successively, di- and monoglycerides, and eventually glycerin and free fatty acids. If a fatty acid component of the glyceride has oxidized, hydrolysis will yield the oxidation product, such as azelaic acid. Ester linkages in the glycerides that have reacted to become part of the polymer matrix also can hydrolyse. Hydrolysis does not affect most of the crosslinks, so fatty acids that have reacted to become part of the polymer matrix will remain attached, although a carboxylic acid group is now present instead of an ester link to glycerin. Such hydrolysis is undoubtedly slow, since the non-polar, hydrophobic polymerized oil matrix does not provide the polar, liquid environment most conducive to hydrolysis, and little water is available to react. If hydrolysis does occur to any appreciable extent during aging, then the resulting polymer consists primarily of crosslinked fatty acids (or their salts) rather than crosslinked glycerides.

Evidence of hydrolysis can be seen in infrared spectra of oil films and paints. In Figure 1, portions of infrared spectra of one-year-old and 15-year-old linseed oil films and a paint sample from an eighteenth-century panel painting are shown. In the one-year-old linseed oil film, the ester carbonyl peak predominates, with the carbonyl peak from free carboxylic acids forming just a slight shoulder on the ester peak. In the 15-year-old linseed oil film, the acid peak is more pronounced, and forms one broad split

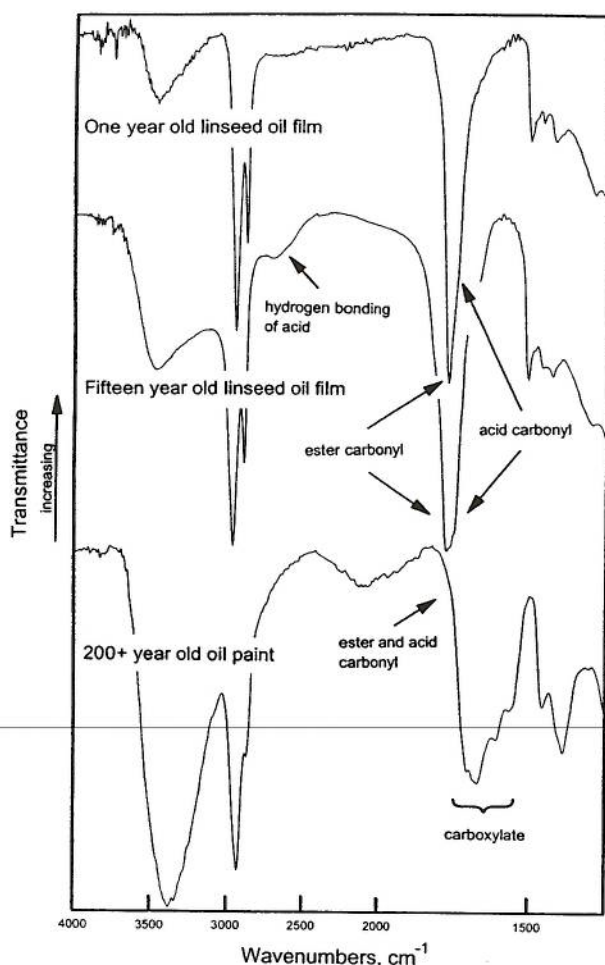


Fig. 1 Infrared spectra of one-year-old and 15-year-old linseed oil films, and a paint sample from an eighteenth-century oil painting. The ester carbonyl peak is supplanted over time by the acid carbonyl peak or, when pigment is present, by carboxylate peaks.

peak with the ester peak. This indicates a relative increase in acid groups compared to the one-year-old film. There is no indication of carboxylate (acid salt) formation, and none would be expected in a pure oil film with no pigment or source of metal ions available. In the 200-year-old paint sample, the ester peak is reduced to just a shoulder, with acid and carboxylate peaks now dominating. Though not quantitative, the spectrum indicates that most of the free acid groups have reacted with the pigment in the sample to form salts. This is not surprising, since pigment makes up a large portion of the paint volume.

Formation of soaps

Free carboxylic acids in the oil can react with metal ions from the pigment to form soaps. The free acid groups of the polymer matrix that are formed by hydrolysis also can react with metal salts to form the corresponding metal 'soap' of the acid. This is especially true for alkaline pigments, which may also accelerate the formation of soaps by catalysing hydrolysis and making more free acids available. Alkaline pigments will not react completely with all available acids, however, and some free fatty acids can always be extracted.

Evaporation of low molecular weight components

Many of the components of oil films, such as fatty acids and their decomposition products, have appreciable vapour pressures and may evaporate from the surface of the paint layer. There have been a number of reports of these materials forming hazy films

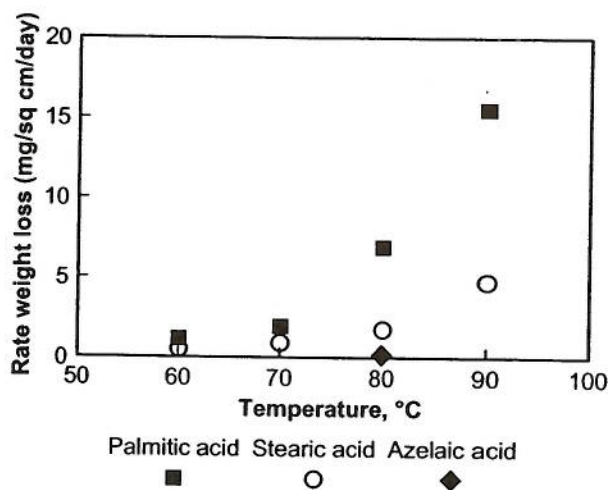


Fig. 2 Evaporation rates of stearic acid and palmitic acid as a function of temperature. The evaporation rate of azelaic acid at 80°C is also plotted. It is only one-tenth and one-fortieth the rates of the fatty acids, respectively.

on the glazing covering paintings, even though the glass was not in contact with the paint. These layers consist primarily of saturated fatty acids. Such examples are not common even in paintings that have been glazed for long periods of time, however, and the phenomenon may be related to exposure of paintings to higher than normal temperatures. This process can be simulated in the laboratory by heating oil paint layers covered by sheets of glass [2]. Azelaic acid, too, was found in the experimental condensates, but in significant amounts only when the sample was also exposed to light. The same article reports results from thermogravimetric analyses indicating that the volatility of azelaic acid is between the values for stearic and palmitic acids. However, those results were extrapolated from elevated temperatures well above the melting point of azelaic acid (106.5°C [3]). Measurements of the evaporation rates of these compounds at lower temperatures (below the melting point of azelaic acid) indicate that nearer normal room temperature, azelaic acid is about one-tenth and one-fortieth as volatile as palmitic and stearic acids, respectively (Fig. 2). Palmitic and stearic acid may not be appreciably volatile at normal room temperatures, either, since even the relatively low temperatures at which these evaporation rates were measured were close to their melting points (63 and 72°C, respectively). This explains the relative absence of azelaic acid from evaporates naturally occurring on older paintings. In the case where azelaic acid was found experimentally, at least some of the azelaic acid (and other diacids) may have formed *in situ* from the photo-oxidation of fatty acids that had already evaporated and condensed on the glazing.

Relative rates of hydrolysis and evaporation

In Figure 3, gas chromatograms of acetone (propanone) extracts of samples of oil paint are presented. It can be seen that in a six-year-old dry but relatively unaged paint film of malachite in cold-pressed linseed oil there are substantial amounts of free fatty acids, as well as significant amounts of glycerides. The same compounds can be seen in the extract of a paint sample from an eighteenth-century panel painting, but the relative amounts are quite different. The amounts of glycerides are greatly reduced due to hydrolysis, as indicated also by the relative increase in the amount of free glycerin. The free fatty acids resulting from hydrolysis are present in substantial quantities, indicating that evaporation is a much slower process than hydrolysis during normal aging. Note that these free fatty acids have not been converted to soaps. Also note that the ratio of palmitic to stearic acid

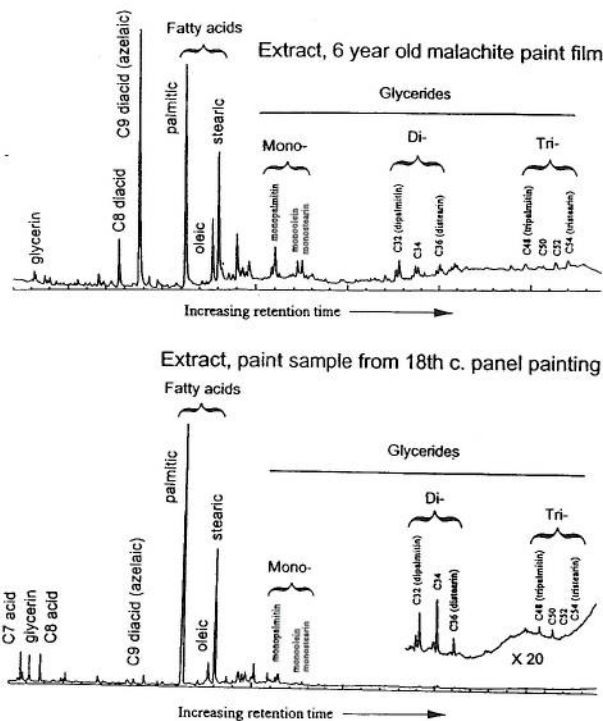


Fig. 3 Gas chromatograms of acetone extracts of a six-year-old sample of malachite in cold-pressed linseed oil and a paint sample from an eighteenth-century panel painting. The glycerides are greatly reduced in the older painting relative to the fatty acids, presumably due to hydrolysis. The ratios of palmitic and stearic acids to the glycerides and to each other indicate that evaporation of the fatty acids is much slower than hydrolysis of the glycerides.

is as expected in a drying oil. If evaporation were occurring at an appreciable rate, the greater volatility of palmitic acid would have resulted in a (relative) decrease in the palmitic:stearic acid ratio. Significant evaporation rates coupled with preferential evaporation of palmitic acid also would imply that the palmitate:stearate ratio of the total acid content (free plus esterified) would decrease. On the contrary, palmitate:stearate ratios in old paint samples are used in identification of the oil type, and fall within the expected ranges of the commonly used oils regardless of age. Evaporation would be further slowed by the presence of a varnish layer.

Even though much of the glyceride reserve of saturated fatty acids in the old paint sample is gone, free fatty acids would be expected to be present in substantial amounts for a long time. In addition, the crosslinked triglycerides also serve as a 'reservoir' of saturated fatty acids, and hydrolysis of ester linkages in the polymer matrix may be slower than that for the mobile, uncrosslinked glycerides. One indication that the polymer matrix itself is slower to hydrolyse than the uncrosslinked glycerides is that paint samples must be exposed to a reagent such as strong alkali to disintegrate and dissolve them. This reaction is used when analysing the total fatty acid content of oil paint samples. It is unclear why this would happen (or be necessary) if the paint sample were already hydrolysed.

The reserves of ester-linked fatty acids will be depleted at some point, and total evaporation of the fatty acids might eventually occur. At this point there will be little extractable material remaining in the paint. This loss of low molecular weight material will over time result in an increasingly stiffer, more brittle film [4]. This is an extremely slow process, however, and takes many centuries. Significant quantities of free fatty acids and glycerides are still present in centuries old films and hydrolysis itself may take hundreds of years to complete [4, 5].

Extraction of soluble components during cleaning and application of varnish

There have been numerous studies on the nature and amounts of materials extracted from oil paint films during cleaning or exposure to solvents. All of the expected compounds, from glycerin to triglycerides, have been reported [4]. Such compounds function as plasticizers, and the extraction of more than a minimal amount of material results in a stiffer, more brittle film, with longer exposures producing greater effects [4]. There is some selectivity of extracted compounds based on polarity [6], but most solvents extract the smaller fatty acids more quickly than the larger glycerides.

Hydrolysis of unextracted glycerides and saturated fatty acids bound to the polymer matrix will eventually replace some of the extracted material, but very slowly and maybe not before the painting is treated again. Most of the extractable and potentially extractable (after hydrolysis) material will eventually be gone, either by exposure to solvents or by evaporation.

THERMAL AGING OF OIL PAINTS

Dry oven aging

Figure 4 shows a gas chromatogram of the total extract of a sample of the same six-year-old paint as in Figure 3, but after aging in an unhumidified dry oven at 80°C for 12 days. There are obvious differences after thermal aging. The most striking are the relatively lower amounts of free fatty acids relative to the glycerides and azelaic acid. Since the amount of triglycerides could only be expected to decrease, this must be due to a reduction in the amount of fatty acids. Since no increase in degradation products is seen (azelaic acid is a specific degradation product of

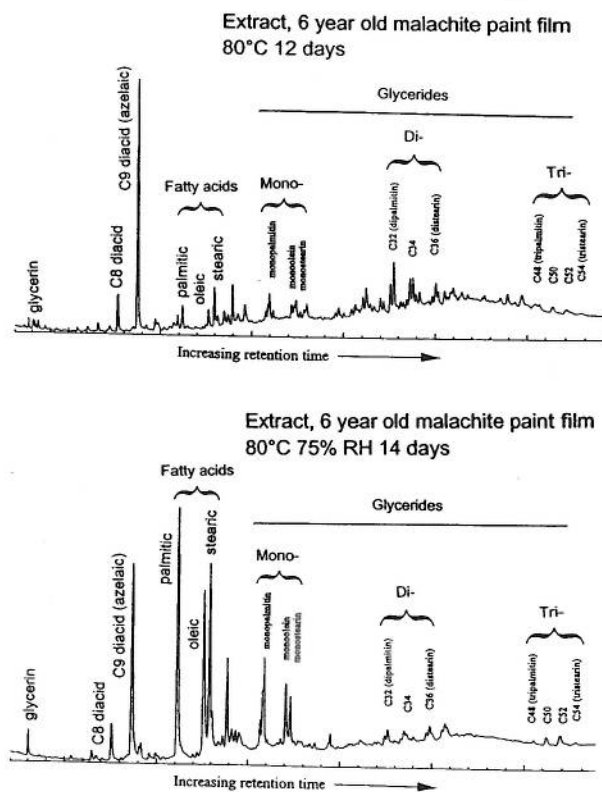


Fig. 4 Gas chromatograms of acetone extracts of the malachite paint from Figure 3 after aging for 12 days at 80°C in an unhumidified oven or for 14 days at 80°C and 75% relative humidity. Dry oven aging depletes the fatty acids (palmitic acid preferentially) through evaporation but induces little hydrolysis. Aging at the higher relative humidity increases the rate of hydrolysis so that it is comparable to the rate of evaporation, but hydrolysis is still not the dominant process that it is during natural aging.

Table 1 Melting points of selected fatty acids and glycerides.

| Compound | Melting point, °C |
|---------------------------|-------------------|
| Azelaic acid | 106.5 |
| Palmitic acid | 63 |
| Stearic acid | 71.5-72.0 |
| Glycerol, 1-monopalmitate | 71-72 |
| Glycerol, 2-monopalmitate | 74 |
| Glycerol, 1-monostearate | 76-77 |
| Glycerol, 1,2-dipalmitate | 69.0-69.5 |
| Glycerol, 1,3-dipalmitate | 72-74 |
| Glycerol, 1,3-distearate | 79.1 |
| Glycerol, tripalmitate | 44.7 |
| Glycerol, tristearate | 55 |

From [3]. Values from other sources may vary depending on purity, crystallization method and so on, but are in the same general range.

unsaturated fatty acids), the obvious explanation is evaporation of these materials. A preferential evaporation of palmitic acid relative to stearic acid would be expected. Indeed, the palmitic:stearic acid ratio falls from 1.4 to 0.62. The rate of evaporation is obviously much faster than any 'replacement' of free fatty acids by hydrolysis, or any other mechanism that would tend to maintain the palmitic:stearic ratio. This is in contrast to naturally aged films in which substantial amounts of free fatty acids remain even when the glyceride reservoir is almost depleted. Thermal aging under dry oven conditions speeds up the process of evaporation by a much larger factor than it speeds up hydrolysis. The loss of compounds that act as plasticizers produces a paint film that is stiffer and more brittle, but through a process that is entirely unlike that of natural aging.

The increase in azelaic relative to palmitic and stearic acid indicates that it does not volatilize from paint at 80°C as quickly as either palmitic or stearic acid, as predicted by measurements at this temperature. The aging temperature of 80°C is below the melting point of azelaic acid, but above those of stearic and

palmitic acids. It is also above those of a number of the other extractable components of paint (Table 1).

Further evidence for the evaporation of material during thermal aging is seen in the results of differential scanning calorimetry (DSC). Figure 5 shows the DSC results for a sample of titanium dioxide in cold-pressed linseed oil, a sample of the same paint aged for 14 days at 80°C and 75% RH, and a sample of the same paint exhaustively extracted with acetone. The untreated sample has thermal absorption maxima at 85 and 75°C, with shoulders at lower temperatures. These probably correspond to phase transitions of the fatty acids and glycerides that have melting points in this general range of temperatures (Table 1). If this material is extracted in acetone, the peaks and shoulders disappear. The same curve is seen for the heated sample, implying that heating also removes the material responsible for the thermal absorption.

Thermal aging at elevated relative humidity

Figure 4 also shows a chromatogram of the same paint aged for 14 days at 80°C but under conditions of high relative humidity (75%). This should speed up the process of hydrolysis but have little if any effect on the rate of evaporation of free fatty acids. Indeed, the palmitic:stearic ratio is not significantly less than that of the unheated paint (1.36 as opposed to 1.39), indicating that the preferential evaporation of palmitic acid is at least partly compensated for by free fatty acids produced by hydrolysis, presumably in the original palmitic:stearic ratio. Hydrolysis is also evidenced by the relative increase in monoglycerides relative to di- and triglycerides. In fact, the rate of hydrolysis is probably comparable to that of evaporation, since the ratio of free palmitic acid to total glycerides remains about the same (0.66 before, 0.71 after). There is a decrease in the palmitic:monoglycerides ratio, however, since monoglycerides now form a larger proportion of total glycerides.

Even at higher relative humidity, the rate of hydrolysis is only comparable to the rate of evaporation, not significantly faster as it is at normal aging temperatures. This difference can be seen in a plot of the ratios of the amounts of palmitic acid to stearic acid, monoglyceride and total glyceride (Fig. 6). Compared to a six-

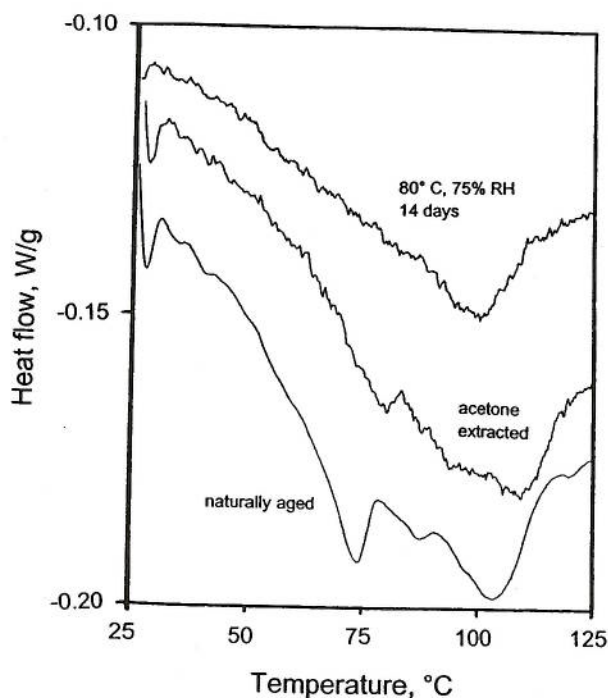


Fig. 5 Differential scanning calorimetry curves for titanium dioxide in linseed oil. The untreated sample exhibits thermal absorption maxima and shoulders at 85°C and below. Extraction with acetone removes fatty acids and glycerides with melting points in this range, and the features disappear. Heating at 80°C and 75% relative humidity also causes these features to disappear, through evaporation of paint film components.

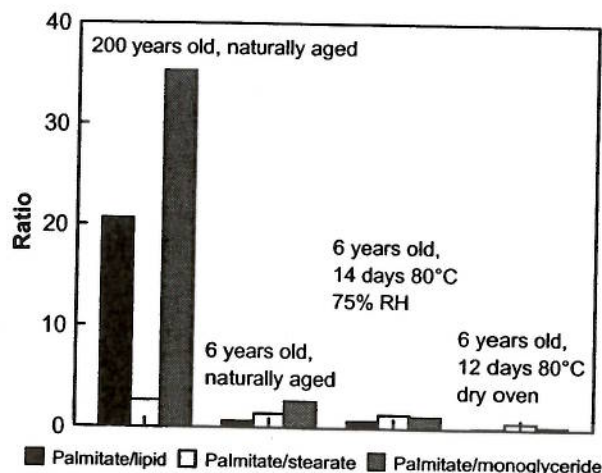


Fig. 6 Ratios of palmitic acid to total glycerides (lipid), stearic acid and total monoglycerides in extracts of a paint sample from an eighteenth-century panel painting, a six-year-old sample of malachite in cold-pressed linseed oil, and the malachite paint after aging at 80°C either in an unhumidified oven or at 75% relative humidity. Loss of glycerides through hydrolysis greatly increases the ratios of palmitic acid to total glycerides and monoglycerides, while thermal aging increases the rate of evaporation of fatty acids so that these ratios are either reduced or merely maintained. Dry thermal aging also reduces the palmitic:stearic acid ratio.

year-old paint sample, hydrolysis in a 200-year-old sample has greatly increased the amount of palmitic acid relative to the glyceride fraction, while thermal aging either reduces or barely maintains the palmitic acid:glyceride ratios, even at high relative humidity. Dry oven aging at 80°C reduces the palmitic:stearic ratio also.

COMPARISON OF NATURAL AND THERMAL AGING

There are significant differences between the processes that take place in paint films at 80°C and at normal room conditions. During natural aging, hydrolysis is the dominant process. At 80°C the rate of hydrolysis is much slower than, or is comparable to, the rate of evaporation of free fatty acids, depending on whether the aging is conducted under dry or humid conditions. Relative humidities higher than 75% may increase the rate of hydrolysis further, but it is not clear that even more extreme conditions would accurately simulate the natural aging process. Thermal aging does result in a stiffer, more brittle paint film, but through a different mechanism than that proposed as causing the embrittlement of very old paint films [5].

Part of the reason for the observed differences may be the fact that the aging temperature is above the melting point of many of the potentially volatile components. The aging temperature is below the melting point of azelaic acid, however. Azelaic acid was the one component, predicted by high-temperature work to be of comparable volatility to the free fatty acids [2], that was not significantly reduced. It may be that aging of paint films conducted above the melting point of important components will not be comparable to natural aging no matter what conditions (besides temperature) are used.

CONCLUSIONS

The aging of paint films at elevated temperatures (80°C and above) is not comparable to natural aging, and is problematic even at lower temperatures if these are above the melting point of paint components. It is possible that lower temperatures combined with moderate to high relative humidities might accurately simulate natural aging, but the temperatures may have to be below the melting points of the fatty acids and glycerides present in the paint. Unfortunately, the rates of reactions at such temperatures are not increased greatly, and the advantages of accelerated aging are considerably diminished. If thermal aging of paint cannot accurately accelerate natural aging to a reasonable rate, research may have to be limited to the use of naturally aged older samples or to extrapolation from results based on naturally aged samples that are 'only' a decade or two old.

The natural aging of oil paints is a complex process, and even now is not understood completely. Simulating long periods of natural aging using short times in the laboratory is not a simple undertaking. Accelerated aging must speed up all aspects of the aging process by the same factor, without introducing new re-

actions, exaggerating minor ones, or diminishing important ones. Unless it can be shown that a specific regime of accelerated aging conditions accurately simulates natural aging for the material being tested, results based on such experiments must be considered suspect. For example, the effects of cleaning will be very different on a paint film from which much of the extractable material that would be present after natural aging has already been removed by heating. The use of materials aged above phase transitions (melting point, glass transition temperature) of their components is especially questionable.

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REFERENCES

- 1 Schilling, M.R., Khanjian, H.P., and Carson, D.M., 'Fatty acid and glycerol content of lipids; effects of ageing and solvent extraction on the composition of oil paints', *Technique* 5 (1997) 71-78.
- 2 Schilling, M.R., Carson, D.M., and Khanjian, H.P., 'Gas chromatographic determination of the fatty acid and glycerol content of lipids. IV. Evaporation of fatty acids and the formation of ghost images by framed oil paintings' in *ICOM Committee for Conservation 12th Triennial Meeting*, Lyon (1999) 242-247.
- 3 Grasselli, J.G., and Ritchey, W.M., (editors), *CRC Atlas of Spectral Data and Physical Constants for Organic Compounds*, 2nd edn, CRC Press, Cleveland (1975).
- 4 Tumosa, C.S., Millard, J., Erhardt, D., and Mecklenburg, M.F., 'Effects of solvents on the physical properties of paint films' in *ICOM Committee for Conservation 12th Triennial Meeting*, Lyon (1999) 347-352.
- 5 van den Berg, J.D.J., van den Berg, K.J., and Boon, J.J., 'Chemical changes in curing and ageing oil paints' in *ICOM Committee for Conservation 12th Triennial Meeting*, Lyon (1999) 248-253.
- 6 Sutherland, K., and Shibayama, N., 'The components of oil films extracted by organic solvents' in *ICOM Committee for Conservation 12th Triennial Meeting*, Lyon (1999) 341-346.

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