

Abstract

Oil paint films were exposed to solvents including toluene, acetone, and triethanolamine for varying lengths of time. Weight measurements show that evaporation of the volatile solvents acetone and toluene from paint films is essentially complete within hours. These dried films weigh less due to extraction of components including glycerol, azelaic acid, fatty acids, and mono-, di-, and triglycerides. Stress-strain measurements show measurable changes in stiffness in bulk films after as little as 30 seconds exposure to the volatile solvents. Dried films are stiffer and somewhat more brittle than unexposed films due to the loss of plasticizing compounds. The ability of paint films to safely tolerate moderate ($\pm 15\%$) fluctuations in relative humidity as one layer in a painting is unaffected. In contrast, the nonvolatile solvent triethanolamine (TEA) does not evaporate appreciably even after two weeks. Exposure to TEA results in a permanent decrease in stiffness.

Keywords

paint, solvent, cleaning, physical properties, weight, stiffness, elasticity, plasticity

Effects of solvents on the physical properties of paint films

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Introduction

It is standard practice to use solvents to remove coatings and dirt from paintings. Many of the effects of solvents on paint films have been examined in numerous studies (Stolow 1985; Erhardt and Tsang 1990; Phenix 1998; White and Roy 1998). Changes in volume, weight, optical appearance, and bulk composition have been examined, as well as the composition of materials leached from the paint. However, little if any work has been conducted on the effects of solvents on critical mechanical properties such as strength, stiffness, elasticity, and plasticity. Though the optical appearance of a paint film is paramount, other physical properties are critical to the long-term survival of a painting during handling, transport, or environmental changes. The elasticity of a paint film (its ability to be reversibly stretched or compressed within a finite range) is especially critical because of the differential dimensional response to environmental changes of the other layers within a traditional painting. This paper examines the effects of selected volatile and nonvolatile solvents as a function of time of exposure, time after exposure, and amount of residual solvent.

The samples

The tested samples consisted of naturally aged, 0.1 to 0.2mm thick, dried oil paint films ranging in age from 6–20 years old. The newer films were made from custom-prepared paints containing only oil and pigment, the older films were prepared from artists' quality commercial oil paints. The films contained various pigments as noted in the text and figures. The mechanical tests required free paint films of a consistent thickness and suitable size, which excluded the use of samples from paintings. Accelerated aging was not used for several reasons. First, previous tests on the older samples had shown that their bulk physical properties had stabilized and become uniform within three years, indicating that the "drying" process for all of the samples would be complete (Mecklenburg and Tumosa 1991). Any subsequent changes due to degradation processes would be incrementally small rather than fundamental. Second, it has not been shown that any accelerated aging process accurately simulates the natural aging of bulk paint films. Light aging probably simulates accurately many of the changes that occur on the surface of paint, but has no significant effect on the interior of bulk samples. Thermal aging causes changes in the interior of paint, but it is questionable if these changes accurately simulate natural aging. The drying and aging process of paint films includes chemical changes such as polymerization, chain scission, oxidation, and hydrolysis as well as physical changes such as the loss of volatile compounds and the "ordering" of polymer chains in thermodynamically stable, compact, pseudo-crystalline arrangements. It is unlikely that elevated temperatures speed up all of these processes uniformly. This is certainly not true if thermal aging is used before the drying process is complete, since it is known that the thermal polymerization of drying oils occurs through a completely different mechanism than the oxidative polymerization of oil films painted out and exposed to air.

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Even if the paint is "dried" before thermal aging, it is unlikely that thermal aging accurately simulates natural aging. For example, natural rubbers form ordered regions ("crystallize") during natural aging. Exposure to elevated temperatures not only prevents the formation of such regions, but can actually reverse the process! It is likely that thermal aging of dried oil paint films would also cause changes in the physical, as well as chemical, aging process. For example, the saturated fatty acids stearic and palmitic, as well as the mono-, di-, and triglycerides containing them, are found in significant quantities even in old paint films (vide infra). The melting points of most of these compounds are in the range 60 to 80° C. Temperatures this high are often used for artificial aging in order to produce changes in a reasonable length of time. However, we have found that changes induced in oil paint films by treatments at such temperatures are quite unlike those seen in naturally aged samples as old as 200 years.

The problems associated with conducting aging experiments above critical phase transitions have been discussed elsewhere (McCormick-Goodhart 1995). It is not a simple matter to demonstrate the equivalence of natural and artificial aging (Erhardt and Mecklenburg 1994), and thus far it has not been done for the thermal aging of paint. We therefore chose to conduct our work on reasonably old naturally aged films.

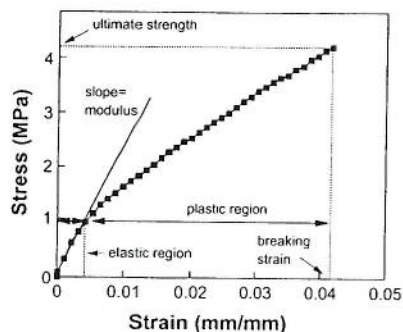


Figure 1. Stress-strain curve for an untreated, eight-year-old paint film prepared from lead white in acid refined linseed oil. The force per cross-sectional area (stress) is plotted as a function of dimensional change (strain). The initial linear portion of the curve defines the elastic (reversible) region, the slope of this area is the modulus, or stiffness. The later portion of the curve represents the plastic region in which permanent deformation occurs. The end of the curve is the breaking point. Measurements conducted at 23°C and 48% RH.

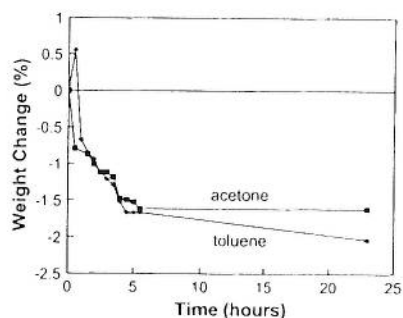


Figure 2. Weight changes over time for samples of a six-year-old paint film prepared from malachite in cold pressed linseed oil after immersion for one minute in toluene or acetone. Measurements conducted at 23°C and 48% RH.

The experiments

A strip of paint film was dipped in a solvent for a measured length of time, removed, and air dried. A different paint sample was used for each combination of solvent, exposure time, and drying time. The films were weighed before and after exposure, and during drying. Stress-strain measurements were conducted either after one hour or after at least 24 hours (the weights had all stabilized within 5 hours). The methods used for these measurements have been described previously (Mecklenburg and Tumosa 1991).

The interpretation of stress-strain data

A typical stress-strain curve for an untreated paint sample (See Fig. 1) provides a number of types of information. The curve plots the amount of strain (dimensional change) and the corresponding stress (force per unit cross-sectional area). The initial linear section of the curve is the elastic region. In this region, the paint recovers and returns to its original size when the force is removed. The slope of this linear section of the curve is the modulus, or stiffness. The subsequent curved and less steep region of the plot is the plastic region, in which the paint has been irreversibly stretched and will only partially recover if the force is released. Materials with little or no plastic region are considered to be "brittle" and their physical strength is quite sensitive to small defects. A stress-strain curve for a paint more brittle than that in Figure 1 would have a similar curve that simply ended earlier. A stiffer paint would have a steeper slope at the beginning of the curve. The end of the curve is where the sample breaks, and represents the maximum possible stress and stretch the paint can take (ultimate strength and breaking strain, respectively). Oil paints have elastic limits, or yield points, similar to those of many other materials, and typically can be reversibly stretched by about a 0.4% change in dimension. Paint also has a significant plastic region, and can be deformed quite a bit before breaking. With proper care and under reasonable environmental circumstances, paint should never leave the elastic (reversible) region, since either improper handling or quite wide environmental changes are required to produce irreversible strains in paint (See Erhardt et al. 1997 and references therein for discussions of calculating allowable relative humidity ranges).

Weight changes

Weight changes resulting from solvent exposure for a six-year-old paint film of malachite in cold-pressed linseed oil are typical of those found (See Fig. 2). Acetone evaporates quickly (at least from and near the surface), and only a weight loss resulting from the extraction of leachable components is seen. The weight

continues to decrease over time as absorbed acetone migrates to the paint surface and evaporates. The weight eventually stabilizes within about five hours. Weight losses for acetone exposure of various paints ranged from about 0.7 to 3%. Toluene produces similar results, although there is a fleeting weight gain that is probably due to the slow evaporation of toluene from and near the surface. Loss of the absorbed acetone and toluene occurs at a similar rate, probably because the rate-controlling step is migration through the paint film and not the volatilization of the solvent. Weight losses for the toluene exposure of various paints ranged from about 0.5 to 4%. (Acetone and toluene have different solvent properties, but are similar in their ability to swell paint films (Phenix 1998). The effect of the nonvolatile solvent triethanolamine (TEA) is quite different. Even though TEA is quite effective in extracting material from paint films (Erhardt and Bischoff 1994), only a weight gain of about 4% was seen. There was no significant change in the weight even after hundreds of hours. TEA is absorbed quickly, and does not evaporate under any reasonable conditions.

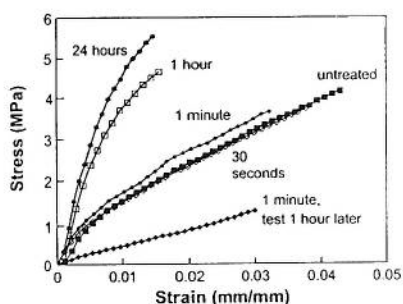


Figure 3. Stress-strain curves before and after immersion in toluene for an eight-year-old paint film prepared from lead white in acid refined linseed oil. Times given are length of immersion. Treated samples were tested at least 24 hours after treatment except as noted. Measurements conducted at 23°C and 48% RH.

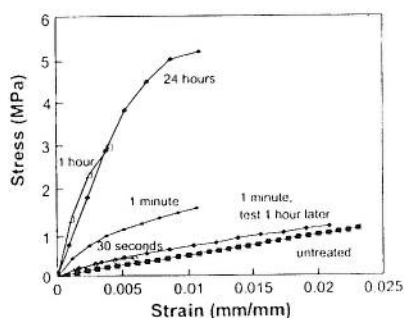


Figure 4. Stress-strain curves before and after immersion in toluene for a six-year-old paint film prepared from malachite in cold pressed linseed oil. Times given are length of immersion. Treated samples were tested at least 24 hours after treatment except as noted. Measurements conducted at 23°C and 48% RH.

Stress-strain measurements: effects of volatile solvents

Results for the treatment with toluene of a paint consisting of lead white in acid-refined linseed oil illustrate the effects of volatile solvents on stress-strain properties (See Fig. 3). All tests except as noted were run more than 24 hours after exposure when the weight had stabilized. The untreated sample has a yield point (elastic limit) of about 0.4%, but does not fail until stretched by over 4%. A 30-second exposure to toluene produces little if any change. Slight differences in breaking length probably are due to sample variation, and are not considered significant. A one-minute exposure does produce a slight increase in the modulus (stiffness). A one-hour exposure produces a significant increase in stiffness and a decrease in elasticity (increase in brittleness) with the breaking strain reduced to about 1.5%. Longer exposure (up to 24 hours) produces only slightly more change. Low-molecular weight components of the paint film act as plasticizers, softening the paint film and extending its plastic region. The extraction of increasing amounts of these materials with longer exposure times results in a stiffer and more brittle paint film. This effect is limited, though, and seems to be essentially complete within an hour. This probably represents the time required to remove completely the leachable components from the tested film. The properties of the completely leached film probably represent the limit that the paint will reach and still remain a viable paint film. It probably also represents a limit for the properties of paint films that have lost volatile components over time. It is significant that even the completely leached film retains most of its elastic region and a significant portion of the plastic region. This leached film is able to safely tolerate quite wide environmental extremes, much as a new paint film. Results for the same paint treated with acetone were quite similar, again emphasizing the similarities in effect of toluene and acetone.

The sample tested one hour after a one-minute exposure is noticeably less stiff. In this case, weight measurements showed that about half of the absorbed toluene was still present, and this residual solvent is evidently enough to have a quite noticeable plasticizing effect. This effect disappears completely after the absorbed toluene has evaporated, and no significant residual effect is seen when the exposure time is short enough.

Results for other paint samples treated with acetone and toluene were similar, though not identical. The degree of stiffening of the paints varied, as did the time it took for them to be affected. A six-year-old film of malachite in cold pressed linseed oil, for example, exhibited significant increases in stiffness with only 30-second exposures (See Fig. 4). A film exposed for one minute to acetone was already stiffer after one hour than the untreated film even though residual acetone was still present. The film stiffened considerably more as the remaining acetone was lost, and eventually was several times stiffer than the untreated film. An 18-year-old paint containing burnt umber in linseed oil behaved similarly. In general, although the specific sensitivity of each paint film varied, the overall effects were similar for all of the samples, as were the effects of acetone and toluene on a specific film.

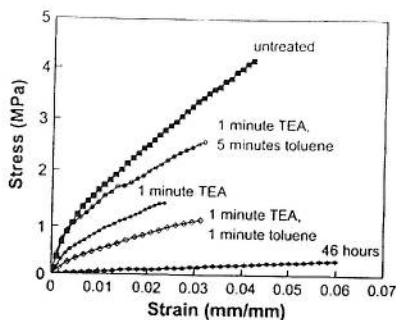


Figure 5. Stress-strain curves for an eight-year-old paint film prepared from lead white in acid refined linseed oil. Treated samples were immersed in triethanolamine (TEA) for the given time, some samples were subsequently also immersed in toluene. Tests were conducted at least 24 hours after treatment. Measurements conducted at 23°C and 48% RH.

The only anomalous results were obtained for an eight-year-old paint consisting of synthetic ultramarine in cold-pressed linseed oil. This paint was relatively unaffected by 30-second and one-minute exposures to toluene (although it was less stiff until the residual toluene was lost), but was stiffened considerably after only thirty seconds exposure to acetone. Long term exposures (one and 24 hours) to acetone also produced more stiffening than the same exposures to toluene. The stiffening effects of acetone had leveled off after one hour. The stiffening effect of toluene was still increasing between one and 24 hours, but appeared to be approaching the same limit as that of acetone. This indicates that the differences are probably due to faster action by acetone, rather than a significant difference in the ultimate sensitivity of the paint to the two solvents.

Stress-strain measurements: effects of a nonvolatile solvent

The effects of TEA on the physical properties of the paint films were drastically different, as would have been predicted by the weight measurements. Treatment with TEA resulted in a softer and more flexible film (as did treatment with toluene and acetone before they evaporated), but the effect was permanent. A white lead paint exposed to TEA lost half its stiffness after only one minute of exposure, a 46-hour exposure left it quite stretchy but extremely weak (See Fig. 5). It is not easy to remove the TEA. A one-minute exposure to TEA followed by a one-minute exposure to toluene removes some of the TEA, but the film is still much less stiff than the untreated film. Even though it is a viscous and slowly diffusing material, TEA was absorbed quickly enough that even a five-minute exposure to toluene was not enough to "clear" the TEA absorbed by the paint film in a one-minute exposure. It is still significantly less stiff than the untreated film. Once TEA is absorbed, it cannot be removed by any technique that would not also significantly alter the paint film.

The nature of the extracted materials

The low molecular weight materials (fatty acids and smaller) extracted from dried oil paint films have been analyzed in previous studies (See, for example, Stolow 1985; Erhardt and Tsang 1990). Predictably, the extracts included free fatty acids, as well as smaller compounds such as oxidation and scission products resulting from the polymerization process. Stolow (1985) used comparisons of the types and amounts of low molecular weight materials in both the original extracts and hydrolyzed extracts to conclude that larger moieties such as triglycerides also were extracted. This is indeed true. A gas chromatographic analysis of the volatile components up to and including triglycerides leached from a six-year-old malachite film by acetone shows that significant amounts of mono-, di-, and triglycerides are extracted, as well as fatty acids and polymerization and degrada-

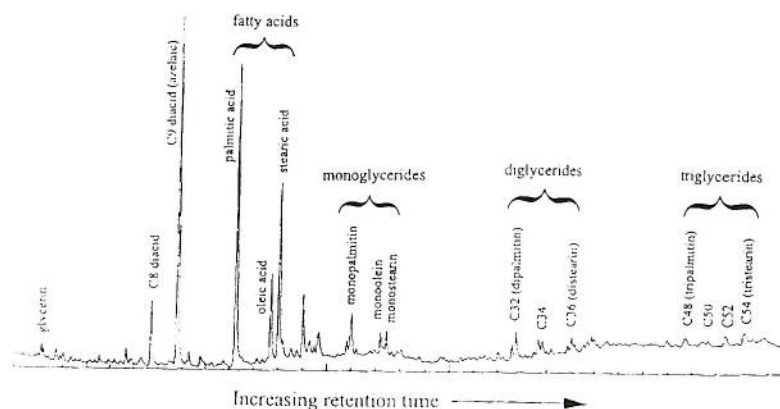


Figure 6. Gas chromatographic analysis of the acetone extract of a six-year-old paint film prepared from malachite in cold pressed linseed oil. Numbers refer to the carbon chain length of acids and diacids, or to the total number of carbons in the fatty acid components of the glycerides. Denaturable compounds analyzed as the trimethylsilyl derivatives.

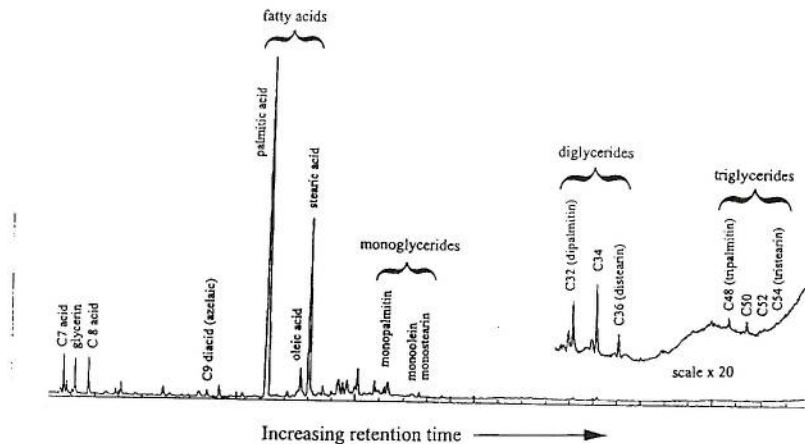


Figure 7. Gas chromatographic analysis of the acetone extract of a paint sample from a fragment of an 18th-century panel painting. Numbers refer to the carbon chain length of acids and diacids, or to the total number of carbons in the fatty acid components of the glycerides. Derivatizable compounds analyzed as the trimethylsilyl derivatives.

tion by-products (See Fig. 6). The amounts of the glycerides decrease in the order mono-, di-, and triglyceride, of course. That is because each successive type is more likely to have contained a polyunsaturated fatty acid that would have been part of the polymerization process and incorporated the glyceride into the polymer matrix. It is primarily the increasingly smaller amounts of mono-, di-, and triglycerides that originally contained only unsaturated fatty acids that can be extracted.

The molecular weight and size also increase in the same order, reducing the extractability. The amounts and composition of such extracts as a function of binder, pigment, solvent, and exposure time will be reported elsewhere. Significantly, such materials also can be extracted from even very old paint films. A sample of oil paint from an 18th-century panel painting still contains extractable glycerides of each type (See Fig. 7). Note also that free glycerol is present in the old paint. Though migration of low molecular weight compounds to the surface of paint films followed by volatilization surely occurs, such results indicate that it is an extremely slow process that would be further inhibited by the presence of a varnish layer.

Summary

Solvents have measurable effects not just on the surface of paint, but also on the physical properties of the bulk film. The initial effect of volatile solvents is softening of the film due to the plasticizing effect of solvent absorbed into the film. This effect lasts until the absorbed solvent has evaporated from the paint film, a process that took a number of hours to complete with the solvents studied. If the exposure was short enough, the paint films recovered within a day and there was no residual effect on the measured properties. Longer exposures ("longer" being as little as 30 seconds depending on the paint and solvent) left the paint films stiffer than untreated films due to the extraction of soluble paint components that had functioned as plasticizers. The loss of plasticizing material could also result in a more brittle film, although the paint films studied retained their elasticity and at least some of their plasticity. A nonvolatile solvent such as TEA permanently softens the paint, and is difficult or impossible to remove completely by subsequent treatment with a volatile solvent. In practice, the presence of cracks and defects in paint film surfaces will magnify the effects of solvents by permitting easier access to the interior of the paint film.

Conclusions

Solvents can affect the bulk physical properties of paint. Short solvent exposure times can temporarily affect a paint film even if there is no permanent change in physical properties. These experiments confirm the obvious, that the temporary presence of absorbed solvent can soften paint layers and make them more

susceptible to mechanical damage during cleaning. Paint films cleaned with volatile solvents should recover within about a day and be at least as stiff as the untreated film after enough solvent is lost. If the solvent exposure is long enough, the resulting extraction of soluble materials leaves the dried film stiffer than before. With short treatment times, the resulting film may be more brittle than an untreated film, but it still retains elasticity and enough plasticity that reasonable handling is safe. Even paint films that have been overcleaned and leached can safely tolerate the same environmental fluctuations as undamaged paint films. This is important, since it is difficult to control solvent exposure times for paintings with cracks and imperfections that absorb and retain liquid solvent. Older paint films that have lost low molecular weight components should also tolerate moderate environmental fluctuations. Nonvolatile solvents should not be used on original paint layers. They permanently soften paint and are not readily removed even with procedures that alone are vigorous enough to alter the paint film.

References

- Erhardt D and Bischoff JJ. 1994. The roles of various components of resin soaps, bile acid soaps and gels, and their effects on paint films. *Studies in conservation* 39(1): 3–27.
- Erhardt D and Mecklenburg MF. 1994. Accelerated vs natural aging: Effect of aging conditions on the aging process of cellulose. In: Vandiver PB, Druzik JR, Madrid JLG, Freestone IC, Wheeler GS, eds. *Materials Research Society symposium proceedings volume 352: Materials issues in art and archaeology IV*. Pittsburgh: Materials Research Society: 247–270.
- Erhardt D, Mecklenburg MF, Tumosa CS, McCormick-Goodhart M. 1997. The determination of appropriate museum environments. In: Bradley S, ed. *British Museum occasional paper number 116: The interface between science and conservation*. London: The British Museum: 153–163.
- Erhardt D and Tsang J. 1990. The extractable components of oil paint films. In: Mills JS, Smith P, eds. *Cleaning, retouching and coatings: Technology and practice for easel paintings and polychrome sculpture*, Preprints of the contributions to the Brussels congress, 3–7 September 1990. London: IIC: 93–97.
- Stolow N. 1985. Solvent action. In: Feller RL, Stolow N, Jones EH. *On picture varnishes and their solvents*. Revised and enlarged ed. Washington, DC: National Gallery of Art: 45–116.
- McCormick-Goodhart MH. 1995. Moisture content isolines of gelatin and the implications for accelerated aging tests and long term storage of photographic materials. *Journal of imaging science and technology* 39(2): 157–162.
- Mecklenburg MF, Tumosa CS. 1991. An introduction into the mechanical behavior of paintings under rapid loading conditions. In: Mecklenburg MF, ed. *Art in transit: Studies in the transport of paintings*. Washington: National Gallery of Art: 137–171.
- Phenix A. 1998. Solvent induced swelling of paint films: some preliminary results. *WAAC newsletter* 20(3): 15–20.
- White R, Roy A. 1998. GC-MS and SEM studies on the effects of solvent cleaning on old master paintings from the National Gallery, London. *Studies in conservation* 43(3): 159–176.

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