

Extraction of Material from Oil Paints by Solvents

David Erhardt, Roland H. Cunningham, and Sirpa Räsänen¹
Smithsonian Center for Materials Research and Education, Smithsonian Institution,
Washington, D.C. 20560, U.S.A.
¹Institute of Arts and Design, Lummetie 2, 01300 Vantaa, Finland

ABSTRACT

Drying oils used to formulate oil paints consist primarily of polyunsaturated triglycerides, along with smaller amounts of mono- and diglycerides, free fatty acids, and other compounds such as sterols. The drying of oils occurs through an oxidative crosslinking process that also produces smaller scission products such as short chain fatty acids and diacids. Compounds that are not attached to the crosslinked oil matrix include glycerin, the unreactive free saturated fatty acids and their glycerides, soaps of fatty acids produced by reaction with metal ions from the pigment, and scission products. As the oil ages, additional soluble material is produced by hydrolysis of glyceride esters. These relatively low molecular weight compounds can be extracted by exposure to solvents, as occurs during the cleaning of paintings. Excessive extraction of material can embrittle the paint film and affect the appearance of the paint. This paper examines the types and amounts of compounds extracted from oil paint films as a function of solvent, exposure time, pigment, and age of the paint. The results indicate that solvents vary more in the speed that they extract material than in their selectivity. The composition of the extracts is consistent with predictions based on the mechanisms of the drying and aging processes. These results confirm the importance of using the least polar solvent possible to clean paintings and to formulate varnishes.

INTRODUCTION

Oil paints are made by combining primarily drying oils and pigments, though lesser amounts of other materials may be added as modifiers. Drying oils are plant-derived oils that polymerize upon exposure to air. When drying oils are mixed with pigments and spread out and exposed to air, the resulting layer polymerizes to form a rubbery, durable colored film. These oil paints have been used for centuries to produce works of art. Varnishes are often used to cover the surface of paintings, serving both to protect them and to saturate the colors. Unfortunately, many of the traditional, as well as newer, varnishes darken over time and must be removed. Other materials also obscure or mar the surface of paintings, including accumulated dirt, soot, and later additions of overpaint or retouchings. Almost every imaginable method and material has been used to clean paintings, including caustic soda, alcohol, ammonia, soap, turpentine, bread, erasers, and recently, lasers. Needless to say, not all approaches are equally successful, and many paintings have been severely damaged. Presently, the use of solvents is the most common method of cleaning oil paintings, having been found in most cases to produce the least visible change when used properly. Solvents do affect the original paint, however, and the choice of solvent(s) and method and time of application generally are chosen to minimize visual changes in the painting. Solvents also affect paintings in other ways, including the removal of low

molecular weight material and a resulting stiffening of the paint layer. Such changes can affect the long term aging of the painting, or make it more susceptible to damage through improper handling or environmental extremes. This paper examines the rate of removal of a number of different compounds as a function of solvent. It also examines the types and amounts of compounds removed from both new and old films and explains the differences in terms of the changes that occur during aging.

The organic components of oil paint films

Drying oils, like other oils and fats, consist primarily of triglycerides. Triglycerides are esters derived from the combination of glycerin (a trifunctional alcohol) and three fatty acids. Most oils and fats contain a number of different types of fatty acids combined with glycerin in a number of patterns. Other species present in oils include mono- and diglycerides, in which only one or two of the alcohol groups in glycerin are esterified with fatty acids, and free glycerin and fatty acids. For example, fresh oils contain a few percent by weight of free fatty acids. Small amounts of other compounds, such as gums, proteins, and sterols may also be present, although they generally either are not removed by the chosen extraction method or are removed during processing. The distinguishing feature of drying oils is that most of the fatty acids are polyunsaturated, containing two or three double bonds. These double bonds are the most chemically reactive moiety in the triglyceride, and readily polymerize when heated or exposed to oxygen. Oxidative scission reactions also take place, however, resulting in small amounts of a number of lower molecular weight species. The most abundant is the nine carbon diacid azelaic acid, formed by oxidation at the usual position of the double bond nearest the carboxylic acid group of the unsaturated fatty acids. Other degradation products include other diacids, alkanes, alcohols, aldehydes, and ketones. Many of the smaller compounds are relatively volatile and are lost through evaporation, while others oxidize further. Of the scission products, the carboxylic acids are the least volatile (and least susceptible to further oxidation), and also may react with pigments to form insoluble non volatile soaps. Other reactions such as hydrolysis of the ester linkages also occur, though quite slowly. Generally, extracts of dried oil films contain primarily free fatty acids, mono-, di- and triglycerides containing only saturated fatty acids (that do not polymerize), short chain acids and diacids, and glycerin.

Figure 1 presents the gas chromatographic separations of extracts of a six year old malachite pigmented oil paint film and a paint sample from a two hundred year old panel painting fragment. These extracts contain free fatty acids, diacids, mono-, di-, and triglycerides, and glycerin. The primary differences between the two are a reduction in the relative amounts of glycerides and an increase in glycerin in the older paint and a reduced amount of extractable azelaic acid. Though the composition of such extracts varies with factors such as the age of the painting, type of pigment and oil, and the presence of additives such as waxes and resins, these results are typical of dried oil paints.

The differences in the extracts of the new and old paint samples are due to changes that occur during aging. Once a drying oil polymerizes through the reaction of its component polyunsaturated fatty acids, most of the glycerides are tied together as the polymeric dried oil matrix. The only compounds that are still extractable are those that do not polymerize, such as

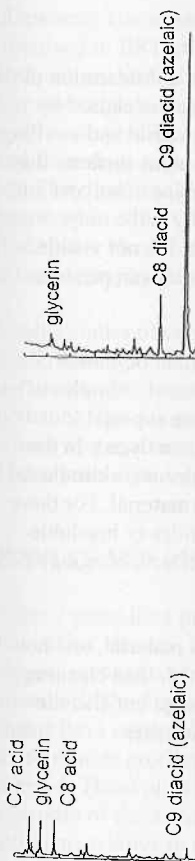


Figure 1. Gas chromatographic separations of extracts of a six year old malachite pigmented oil paint film and a paint sample from a two hundred year old panel painting fragment.

those containing only the degradation products. The composition of the extractable material has been reported [2] to include unreacted fatty acids. Free fatty acids form insoluble soaps. The presence of a high ratio of free fatty acids is indicative of the formation of soaps.

anges can affect
ugh improper
f a number of
ounts of
in terms of the

ides are esters
y acids. Most
lycerin in a
s, in which only
ree glycerin and
acids. Small
resent, although
moved during
ds are
the most
ted or exposed to
l amounts of a
n diacid azelaic
arboxylic acid
diacids, alkanes,
volatile and are
the carboxylic
may react with
s of the ester
contain primarily
s (that do not

ld malachite
painting
erides, and
amounts of
f extractable
s the age of the
nd resins, these

ges that occur
nt
eric dried oil
erize, such as

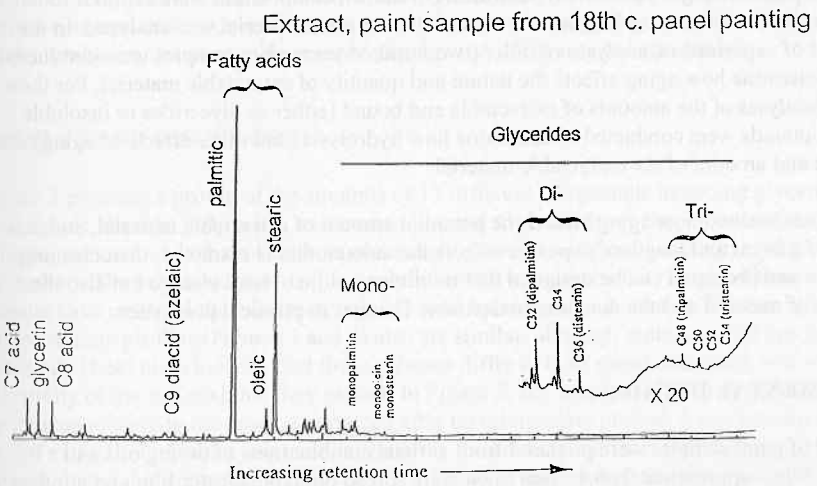
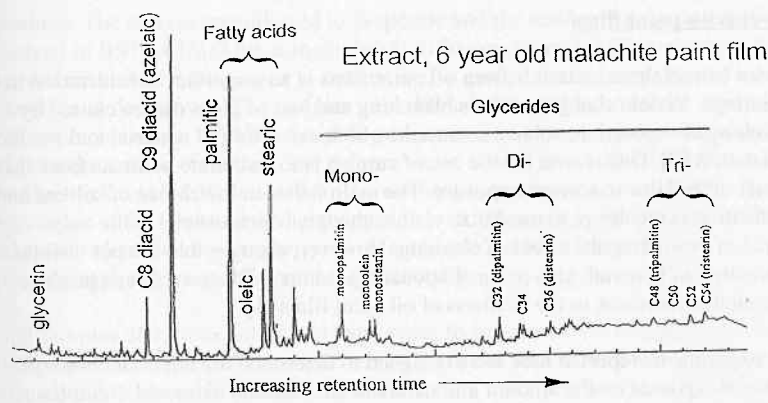


Figure 1. Gas chromatographic analyses of a six year old malachite pigmented cold pressed linseed oil paint film and a paint sample from a two hundred year old panel painting fragment.

those containing only the unreactive saturated fatty acids, and the low molecular weight degradation products. Over time, however, other slower reactions affect the nature and amount of the extractable material. Hydrolysis of glyceride linkages can free up additional fatty acids. It has been reported [2] that hydrolysis of the glyceride esters eventually frees essentially all of the unreacted fatty acids. Free fatty acids can react with metal ions from the pigment to form insoluble soaps. The proportion of material that is extractable depends to a great extent on the ratio of free fatty acids to acids that are bound either by unhydrolyzed ester bonds or by the formation of soaps.

Effects of solvents on paint films

That solvents can extract these materials from oil paint films is an important consideration in the cleaning of paintings. Visible changes such as blanching and loss of gloss can be caused by excessive or prolonged exposure to solvents, caused by both extraction of material and swelling of the dried oil matrix [3]. One reason for the use of varnish is to resaturate paint surfaces that have become mat or dull due to solvent exposure. The main factor in the choice of solvent and method of application is the desire to minimize visible change, which usually is the only available method of evaluating the effect of cleaning. However, changes that are not visible, such as the extraction of material, also occur. Exposures as short as 30 seconds can produce permanent measurable increases in the stiffness of oil paint films [1].

The first set of experiments reported here were designed to determine the effect of choice of solvent and time of exposure on the amount and nature of the material extracted. Samples of previously prepared eight year old oil paint films of known composition were exposed to different solvents for varying lengths of time and the extracted material was analyzed. In the second set of experiments, analyses of older (two hundred year) paint samples were conducted in order to determine how aging affects the nature and quantity of extractable material. For these samples, analyses of the amounts of extractable and bound (either as glycerides or insoluble salts) compounds were conducted to determine how hydrolysis (and other effects of aging) affect the nature and amount of the extractable material.

Once it is understood how aging affects the potential amount of extractable material, and how the type of solvent and length of exposure affects the amount that is extracted, then cleaning procedures and protocols can be designed that minimize not just visual change but also the extraction of material and the resulting undesirable changes in physical properties.

EXPERIMENTAL DETAILS

A number of paint samples were prepared from various combinations of drying oils and pigments. Films approximately 0.15 mm thick were spread out on polyester film and allowed to dry and age at ambient laboratory conditions (22 C, 50% RH). The results reported here are for eight year old films of smalt, a pigment ground from a cobalt blue glass frit, in cold pressed linseed oil (both Kremer Pigmente). Results for other films tested so far vary considerably with the pigment and oil, but display similar trends with solvent type and time of exposure.

Circular samples were punched from the paint-coated polyester sheets. The paint film was left on the polyester sheets. The circular samples were placed in a vial cap (the samples were cut the same size as the cap liner), and placed on a vial containing solvent. The vial was inverted to expose the paint film to the solvent for the chosen time, turned upright, and the cap removed. A known amount of tetratricontane in pentane was added to the vial as an internal quantitative standard. The paint sample was allowed to dry and saved for other measurements to be reported

elsewhere. The solvent was allowed to evaporate and the residue was analysed. The residue was dissolved in BSTFA (*N,O*-bis(trimethylsilyl) trifluoroacetamide) (Pierce) which functions as both solvent and silylating agent to convert active groups to the less polar and more volatile trimethylsilyl derivatives. The samples were diluted with dichloromethane if necessary. Analyses were conducted on an HP 5890 Series II gas chromatograph equipped with on column injection and flame ionization detection. The column was a 15m 0.32mm ID DB1-HT column with 0.1 μ m film thickness (J&W Scientific). The carrier gas was hydrogen at 100kPa. The initial temperature of 50°C was immediately raised by 10°C/minute to 380°C and held for 15 minutes. Peaks were identified by comparison with standards, and verified with gas chromatography/mass spectrometry if questionable.

Small samples of various colors and paint types from several two hundred year old fragments of panel paintings were extracted in acetone for 24 hours. The extract was separated, evaporated, and analyzed as above. The remaining paint sample was hydrolyzed in 10% w/w KOH in methanol. The solution was acidified with HCl, extracted with diethyl ether, and the ether extract was separated, evaporated, and analyzed as above. Ratios of extractable:bound (hydrolyzable) material were determined through use of the internal standard.

RESULTS AND DISCUSSION

Figure 2 provides a profile of the amounts of 17 different compounds including glycerin, short chain acids, diacids, fatty acids, and mono-, di-, and triglycerides in the 30 second hexane, toluene, acetone, and ethanol extracts of the eight year old samples of smalt in cold pressed linseed oil. The profile shapes are the same, but differ in their absolute height. Ethanol and toluene have removed the most material, followed by acetone and hexane. The two minute and fifteen minute profiles (Figures 3 and 4) also are similar, although more material has been removed. These plots indicate that these solvents differ in their speed, but much less so in the selectivity of the material that they extract. In Figure 5, the amounts of each compound extracted by toluene relative to the amount extracted after 60 minutes are plotted. It can be seen that the rate of extraction of each compound is relatively linear. This indicates that the rate of extraction of each material is controlled by the rate of diffusion of the solvent, and the rate at which it swells the paint film, not by the solubility of each compound in the solvent. This interpretation is reinforced in Figure 6, which plots similar data for ethanol. All compounds are rapidly extracted for the first two minutes, after which the rates for each fall off. Though there is some slight selectivity indicated here (as in the previous data), it appears that within the first few minutes ethanol has already extracted much of the available material, and extraction of the remaining material is much slower. This is also indicated in Figure 4, which shows that after fifteen minutes acetone and toluene have begun to catch up with ethanol. Previous experiments indicated that all four solvents ultimately remove similar amounts of material.

Table I lists the percent extractable material for four important components samples of 200 year old oil paint. In fresh oil, almost all of the glycerin and palmitic and stearic acid are present in the form of glyceride esters. Azelaic acid is formed during drying and aging by oxidation of unsaturated fatty acids which also are present mostly as esters, so that when initially formed

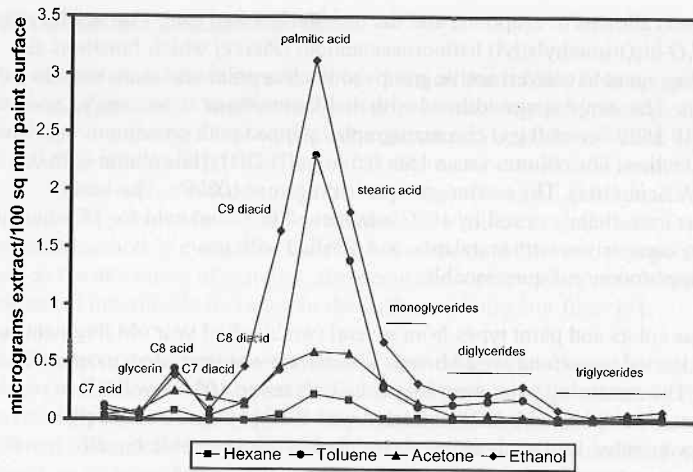


Figure 2. Amounts of compounds extracted from 8 year old small pigmented cold pressed linseed oil paint film samples during 30 second exposures of the surface to hexane, toluene, acetone, and ethanol.

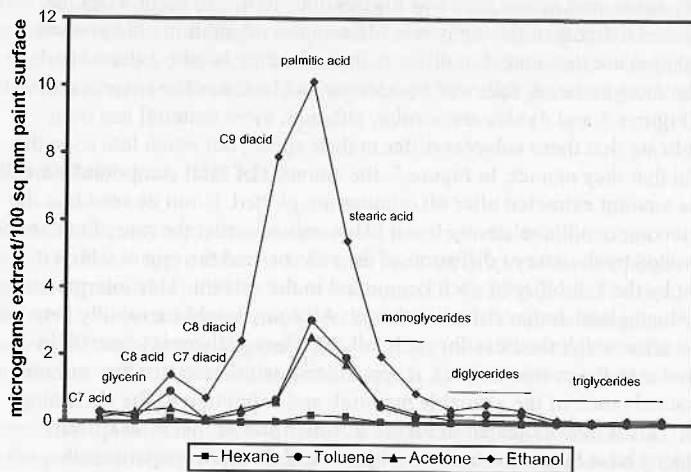


Figure 3. Amounts of compounds extracted from 8 year old small pigmented cold pressed linseed oil paint film samples during 2 minute exposures of the surface to hexane, toluene, acetone, and ethanol.

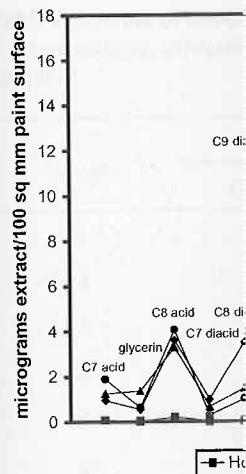


Figure 4. Amounts of compounds extracted from 8 year old small pigmented cold pressed linseed oil paint film samples during 2 minute exposures of the surface to hexane, toluene, acetone, and ethanol.

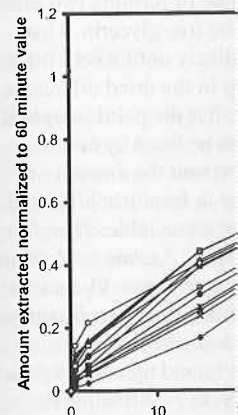


Figure 5. Amounts of compounds extracted from 8 year old small pigmented cold pressed linseed oil paint film samples during 2 minute exposures of the surface to hexane, toluene, acetone, and ethanol, normalized to the amount extracted during 30 second exposures.

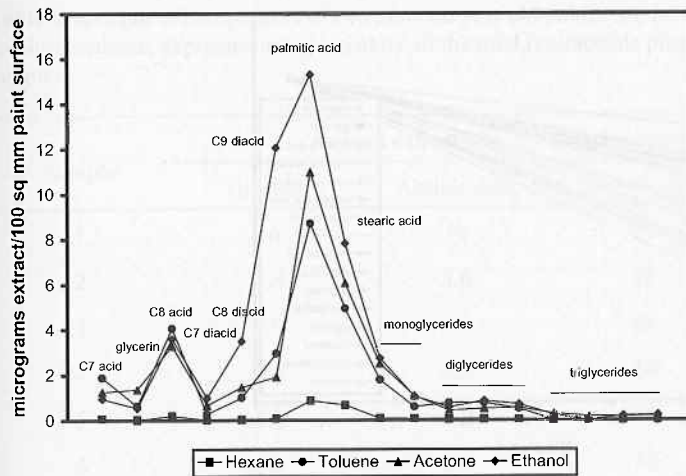


Figure 4. Amounts of compounds extracted from 8 year old small pigmented cold pressed linseed oil paint film samples during 15 minute exposures of the surface to hexane, toluene, acetone, and ethanol.

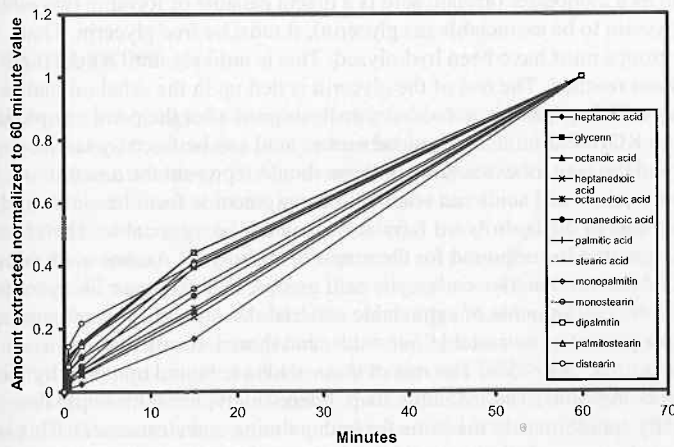


Figure 5. Amounts of compounds extracted from 8 year old small pigmented cold pressed linseed oil paint film samples by toluene as a function of time. Amounts of each compound are normalized to the amount extracted after 60 minutes.

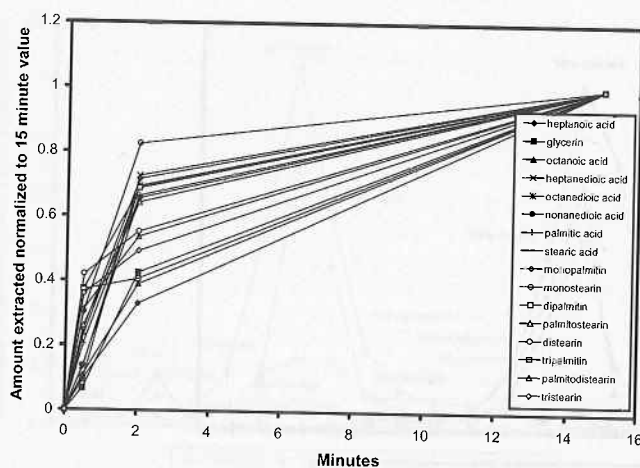


Figure 6. Amounts of compounds extracted from 8 year old small pigmented cold pressed linseed oil paint film samples by ethanol as a function of time. Amounts of each compound are normalized to the amount extracted after 15 minutes.

azelaic acid also is present as a monoester (azelaic acid is a diacid capable of forming two ester and/or salt groups). For glycerin to be extractable (as glycerin), it must be free glycerin. That means that all three ester groups must have been hydrolyzed. This is unlikely until a very high degree of hydrolysis has been reached. The rest of the glycerin is tied up in the dried oil matrix by at least one glyceride ester linkage, and is not seen by analysis until after the paint sample is completely hydrolyzed with KOH. Palmitic, stearic, and azelaic acid can be freed by one hydrolytic reaction each, and the percent extractable of these should represent the amount present as free acid. However, the freed acids can react with the pigment to form insoluble and unextractable soaps. If so, some of the hydrolyzed fatty acids may not be extractable. Therefore, the percent extractable represents a lower bound for the extent of hydrolysis. Azelaic acid, which is smaller, more mobile, and has two reactive carboxylic acid groups, is much more likely to be bound as a soap, as seen in the low amounts of extractable material. Much higher percentages of palmitic and stearic acid are present as extractable free acids, and these indicate minimum values of hydrolysis ranging from 15 to 85%. The rest of these acids are bound up either by the original ester linkage or by conversion to an insoluble soap. Interestingly, in each sample the percent extractable is usually approximately the same for both palmitic and stearic acid. This is chemically reasonable, since both are similarly reactive and susceptible to hydrolysis. However, it also indicates that extensive evaporation of fatty acids has not occurred, because this would have greatly reduced the extractable fraction of the much more volatile free palmitic relative to stearic acid. This is in agreement with earlier experiments, which concluded that evaporation of fatty acids is not a major factor in aging at normal ambient temperatures [4].

Table I. Amount of compounds extracted from 8 year old small pigmented cold pressed linseed oil paint film samples by ethanol as a function of time. Amounts of each compound are normalized to the amount extracted after 15 minutes.

Sample
1
2
3
4
5
6
7
8
9
10

CONCLUSIONS

The extraction of organic compounds from aged paint samples immediately and extractable (shortest time measured) removed by different solvents. The lack of selectivity is probably due to the presence of soluble material. Non-saturated solution, so the limiting factor is the rate of solvent. Ethanol removed material (this fast rate starts to level off) removal of surface material may be removal of material may be matrix. Ethanol, for instance, rate, while toluene mainly continue the initial rate of removal of solvents eventually remove

Table I. Amount of components of two hundred year old paint samples extractable by dichloromethane, expressed as a percentage of the total (extractable plus bound) present in the sample.

Sample	Amount extractable, % of total amount in sample			
	Glycerin	Azelaic acid	Palmitic acid	Stearic acid
1	16	18	85	87
2	5.4	5.0	48	46
3	0.9	0.6	64	75
4	0.6	0.3	14	17
5	3.0	3.0	75	74
6	0.6	2.7	50	61
7	0.1	1.4	45	39
8	1.6	3.7	74	79
9	3.6	5.7	59	62
10	2.0	5.0	64	63

CONCLUSIONS

The extraction of organic compounds from dried oil paint films is a rapid process, beginning immediately and extracting easily measurable amounts of material within 30 seconds (the shortest time measured). The process is relatively unselective, and the "profiles" of compounds removed by different solvents are similar up to one hour (the longest time period measured). The lack of selectivity is probably due to the large amounts of solvent present relative to the amounts of soluble material. None of the compounds are present in quantities great enough to produce a saturated solution, so there is more than enough solvent to dissolve the material present. The limiting factor is the rate at which the solvent gains access. This rate is different for each solvent. Ethanol removes material at an initially faster rate than toluene, acetone, or hexane, but this fast rate starts to level off after a few minutes. This initial fast rate might be due to the removal of surface material or material close to channels around pigment particles. The later removal of material may occur more slowly as the solvent diffuses into and swells the dried oil matrix. Ethanol, for instance, removes material quickly for several minutes, and then at a slower rate, while toluene maintains its initial rate of removal for at least an hour. Slower solvents continue the initial rate for a longer period of time, and, according to earlier experiments, all solvents eventually remove similar amounts of material.

These results correlate with, and may help to explain, results based on practical experience and visual evaluations. Polar solvents such as ethanol often cause blanching. Even though ethanol may not produce as great a swelling of the oil film as intermediate polarity solvents such as acetone or toluene, the quick removal of easily extractable material may produce voids that diffuse entering light and prevent it from interacting with the pigment. Nonpolar solvents such as hexane do not dissolve the available material quickly, and swell the oil film slowly and minimally so that removal of the less accessible material also is slow.

These results also emphasize the importance of using the least polar solvent possible in any treatment of a painting. This is true not only during cleaning, but also during the application of varnish. The most prolonged exposure of a painting to solvent is during the application of varnish, and the use of varnishes that can be applied in nonpolar or only slightly polar solvents should minimize the effect of treatments on paint films.

Long term aging results in a significant increase in the extractable fraction of saturated fatty acids, presumably through hydrolysis of glyceride ester bonds. Hydrolysis also results in a concurrent decrease in glycerides, although significant increases in free glycerin are not seen until hydrolysis is much further along. These free acids can be bound up as nonextractable soaps, as indicated by the low extractable fraction of the difunctional azelaic acid. The increase of soluble material with age makes it even more critical that suitable solvents and treatment methods be used.

REFERENCES

1. C. S. Tumosa, J. Millard, D. Erhardt, and M. F. Mecklenburg, in *12th Triennial Meeting Lyon 29 August - 3 September 1999*, edited by J. Bridgland, (ICOM Committee for Conservation, Brussels, 1999) pp. 347-352.
2. J. D. J. van den Berg, K. J. van den Berg, and J. J. Boon, in *12th Triennial Meeting Lyon 29 August - 3 September 1999*, edited by J. Bridgland, (ICOM Committee for Conservation, Brussels, 1999), pp. 248-253.
3. D. Erhardt and J. S. Tsang, in *Preprints of the Contributions to the Brussels Congress, 3-7 September 1990. Cleaning, Retouching, and Coatings*, edited by J. S. Mills and P. Smith, (The International Institute for Conservation of Historic and Historic Works, London, 1990) pp. 93-97.
4. D. Erhardt, C. S. Tumosa, and M. F. Mecklenburg, in *Preprints of the Contributions to the Melbourne Congress, 10-14 October 2000. Tradition and Innovation: Advances in Conservation*, edited by A. Roy and P. Smith, (The International Institute for Conservation of Historic and Historic Works, London, 2000), pp. 65-69.

Characterization of

C. Montoya, J. Lanás, M. ...
Dept. of Chemistry and ...

ABSTRACT

Ten ancient mortars of ...
María de Zamarrce in Ne ...
and to characterize the t ...
out including: morpholo ...
mineralogical studies (X ...
soluble salts); grain size ...
thermogravimetric anal ...
quartz, as aggregate, has ...
studied samples has con ...
not taken carefully. The ...
related to calcite and do ...
detected. Finally, the ap ...
mixtures are presented.

INTRODUCTION

In some previous pap ...
mortars used by ancient ...
samples of mortars used ...
(1141-1167) have been ...
the type of binder empl ...
(Spain), with a single na ...
Mortars have been exar ...
previous works includin ...
microscopy); mineralog ...
sample; soluble salts ar ...
characterization of the a ...
conclusion being the ap ...
to establish standards f

EXPERIMENTAL

The morphological c ...
magnification x65 (opt ...
in the samples were det ...
D8 Advance diffracton ...
method, with a CuK α ...
The chemical study has ...
flux in order to determi ...
chemical procedures [7 ...
emission spectroscopy ...
Plus Sequential) (Fe, A ...
(Perkin Elmer 460, Üb ...
concentrations of anion ...
Conductivity Detector)

MATERIALS RESEARCH SOCIETY
SYMPOSIUM PROCEEDINGS VOLUME 712

Materials Issues in Art and Archaeology VI

Symposium held November 26–30, 2001, Boston, Massachusetts, U.S.A.

EDITORS:

Pamela B. Vandiver

Smithsonian Center for Materials
Research and Education
Washington, D.C., U.S.A.

Martha Goodway

Smithsonian Center for Materials
Research and Education
Washington, D.C., U.S.A.

Jennifer L. Mass

Winterthur/University of Delaware
Program in Art Conservation
Winterthur, Delaware, U.S.A.



Materials Research Society
Warrendale, Pennsylvania