Solvent extractable components of oil paint films

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5. Extraction of soluble material from a paint film by a varnish solution

Abstract

Experiments were carried out to investigate the extraction of soluble components from a paint film by a solvent based varnish applied to the film. A series of oil paint samples were coated with varnishes formulated with a range of resins and solvents. The extraction of fatty acids from the paint film into the varnish layer was measured by gas chromatographic analysis of the dried varnish film, and of samples of the paint film before and after treatment. The quantities extracted were found to depend not only on the solvent used to apply the varnish, but also on the resin component, with varnishes formulated with more polar, oxygenated resins extracting more than those made from a nonpolar, hydrocarbon resin. The results are interpreted in the context of extraction experiments using free solvents.

5.1. Introduction

Much of the research which has been carried out into the effects of solvents on paint layers has focussed on the effects of free solvents, since these have traditionally been – and remain – the most widely used agents for cleaning paintings.

Another instance in which paintings are exposed to solvents is during the application of a varnish. An investigation by Tsang and Erhardt [1] demonstrated that application of a solvent-based varnish to oil paint films can result in a similar extraction of soluble components as is found with exposure of the paint films to free solvent. This was shown by the detection, using gas chromatography, of fatty acids in dried varnish films removed from paint layers. The varnish was found to act as a poultice, with the solvent diffusing into the paint film and drawing soluble oil components up into the varnish layer. These results reinforced the idea that the choice of solvents for use in the application of a varnish is important, from the
point of view of possible effects on the paint film, in addition to those for use in cleaning treatments [2].

This study was designed to investigate these ideas further, by carrying out a series of tests in which different varnish formulations were applied to an oil paint film, and gas chromatographic analysis was used to determine the quantities of organic material transferred from the paint into the varnish layers. Further alterations in the organic composition of the paint film following subsequent removal of the varnish layers using solvent swabs, in a simulation of cleaning, were also measured.

These experiments were intended to provide some indication of the potential leaching effect of more “realistic” solvent exposures, for comparison with the extraction experiments involving immersion of paint samples in solvent, as described in previous chapters. Additionally, the different varnish formulations were tested to investigate the influence of varnish composition on the leaching process.

5.2. Experimental

5.2.1. Paint film and varnishes

The paint film used in the study was made from sun thickened linseed oil, pigmented with umber, aged 3-4 years (see Appendix 3 for details). This was selected as a uniform paint layer of well defined composition. In addition, this paint formulation has a high medium content, and is relatively slow drying, which means that extraction of soluble components will be exaggerated, and more easily measured than in a fast drying paint with low medium content, such as lead white.

Varnishes were made using the resins Paraloid B-72 (an ethyl methacrylate – methyl acrylate copolymer), MS2A (a chemically reduced ketone resin), Regalrez 1094 (a hydrocarbon resin) and dammar resin. B-72 was dissolved in xylene (2g in 10mL), MS2A and Regalrez in Sol340HT (7.5g in 10mL, and 9g in 10mL, respectively), and dammar in a mixture of Sol340HT and xylene (10g in 7mL Sol340HT/3mL xylene). The xylene used was a mixture of ortho, meta and para isomers. The Sol340HT was redistilled prior to use, to remove components of low volatility which were found to interfere with GC analysis (see Chapter 4, experimental section, for details).

The varnish concentrations were chosen empirically to give solutions of approximately equal viscosity. They were more viscous than would generally be
used in practice: this was to produce thicker films which could be more easily removed from the paint film after drying.

These materials represent resins and solvents with a range of properties: resins which are polymeric (B-72) and low molecular weight (MS2A, Regalrez, dammar); natural (dammar) and synthetic (B-72, MS2A, Regalrez); and solvents with different polarity and aromatic content.

5.2.2. Varnishing and cleaning simulations

Sections of paint film on Mylar, a few square centimetres each, were used for the tests. Small samples of paint were taken from these films, before varnishing, for gas chromatographic (GC) analysis to determine the initial fatty acid levels in the paint film. (Quantitative GC methods are described in detail in Chapter 7.) Varnish was then applied to the paint film in a single coat and allowed to dry.

Fatty acids transferred into the varnish layers were measured in two ways: by analysis of the dried varnish layer, and of the paint layer after mechanical removal of the varnish. For mechanical removal of the polymeric resin, B-72, it was possible to peel away the dry film. For the low molecular weight resins it was necessary to fragment the varnish film using a scalpel blade. Only half of the paint section was cleared of varnish mechanically in each case, with the remainder of the varnish left for removal using solvent.

The mechanically removed resin samples were extracted in solvent to separate the fatty acid components for analysis. Polar solvents were selected in which the resins were predominantly insoluble, but in which fatty acids and glycerides would be readily soluble: ethanol for B-72, and acetone for the other resins (no single solvent was found in which all resins were insoluble, but it was felt that both ethanol and acetone would be effective in removing the bulk of lipid components from the resin samples, and that the results would be comparable). After extraction for 24 hours, the liquid fraction was reduced to dryness under a stream of nitrogen, and analysed using GC.

Samples were also taken from the mechanically cleared paint film for GC analysis, to provide an additional measurement of alterations of fatty acid levels in the paint layer.

The remaining varnish was removed from the paint samples using solvent and cotton swabs, in a simulation of cleaning. The same solvent was used as in the formulation of the varnish, except in the case of dammar, where pure xylene was
used. After allowing the solvent to dry, further paint samples were taken for measurement of the final fatty acid levels in the paint film.

The experimental procedure for the analysis of paint samples at different stages is illustrated schematically in Figure 1 (analysis of dried varnish scrapings was carried out using separate paint samples). Duplicate experiments were generally run for each varnish tested, and averages of results are presented, unless otherwise stated.

**Figure 1**  *Scheme for experiments to measure leaching effects of varnishing and cleaning.*
Extraction of soluble material from a paint film by a varnish solution

It should be noted that the cleaning step in these experiments is not intended to be representative of a typical cleaning procedure. This would be very difficult to achieve, since there is so much variation in practical situations according to factors such as the types of materials used, their age and extent of deterioration. The tests were made to provide a simple, preliminary comparison of the effects of relatively brief, superficial exposures to varnish solutions and free solvent.

In addition, the absolute quantities of fatty acids extracted are unlikely to be representative of any extraction of material that might occur in practice. The paint film used for the test was young (approximately 3 years), and made with a high medium content and relatively slow drying pigment, and will differ from much older paint films in the proportion, and type, of soluble material, as discussed in previous chapters. However, experiments carried out on a uniform and well-defined film allow for controlled comparisons of the relative effects of the different treatments and solvents. Experiments to measure cleaning effects on paintings, dating from the seventeenth to nineteenth centuries, will be described in Chapter 6.

5.3. Results

5.3.1. Analysis of resin samples

The quantities of fatty acids detected in samples of varnish removed from paint films are presented in Figure 2, plotted as micrograms of each fatty acid extracted per square millimetre of paint. Data for the duplicates of each experiment are given in Table 1. These measurements are consistent with the findings of Tsang and Erhardt [1], that exposure of an oil paint film to a relatively small amount of solvent in the form of a varnish can still have a measurable leaching effect.

For each sample, the proportions of palmitic and stearic acids are similar, with P:S ratios of between 1.3 and 1.8. These are consistent with P:S ratios found in the untreated paint samples, and are typical for linseed oil [3].

Clear differences can be seen between the amounts extracted by the different varnishes, with extraction occurring in the order: dammar > MS2A > B-72 > Regalrez. As with the solvent extraction results for this paint film described in Chapter 4, these differences are more pronounced for azelaiic acid.

The differences cannot be explained purely on the basis of the solvent used for the application of the varnish: if this were the case, the Regalrez and MS2A varnishes, being applied in the low aromatic mineral spirit Sol340HT, would be expected to have the least effect. B-72, applied in the more polar, aromatic xylene,
Regalrez and Sol340HT + xylene would have a greater effect; and dammar, applied in a mixture of the two solvents, would have an intermediate effect.

The relative rates of evaporation of the two solvents will have some influence: Sol340HT is a much slower evaporating solvent than xylene, and will therefore stay in contact with the paint layers for considerably longer when applied in a varnish. This does not, however, explain the large differences observed between the results for Regalrez and MS2A, both applied in the same solvent.

**Figure 2** Fatty acids extracted from paint films by different varnish formulations.

**Table 1** Quantities of fatty acids extracted from paint film by varnishes. Results for duplicates of each experiment are shown.

<table>
<thead>
<tr>
<th>varnish</th>
<th>fatty acids detected (µg per mm² paint)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>palmitic</td>
</tr>
<tr>
<td>Regalrez 1094 #1</td>
<td>0.06</td>
</tr>
<tr>
<td>Regalrez 1094 #2</td>
<td>0.05</td>
</tr>
<tr>
<td>Paraloid B-72 #1</td>
<td>0.08</td>
</tr>
<tr>
<td>Paraloid B-72 #2</td>
<td>0.08</td>
</tr>
<tr>
<td>MS2A #1</td>
<td>0.12</td>
</tr>
<tr>
<td>MS2A #2</td>
<td>0.13</td>
</tr>
<tr>
<td>dammar #1</td>
<td>0.12</td>
</tr>
<tr>
<td>dammar #2</td>
<td>0.14</td>
</tr>
</tbody>
</table>

n.d. = not detected
The results therefore appear to be influenced by the resin component of the varnish; this will be discussed in more detail below.

5.3.2. Analysis of paint samples

Samples taken from the paint films for analysis by GC provided an alternative measure of materials extracted from the films. Samples were taken before varnishing; from paint areas which had been varnished and then cleared of varnish mechanically; and from areas which had been varnished and then solvent cleaned using swabs (see Figure 1). Comparisons of fatty acid levels in the different groups of samples allowed estimations of the quantities of the component fatty acids extracted from the paint film by varnishing alone, and by varnishing followed by cleaning (see Chapter 7 for details of quantitative GC analysis).

In the cleaning step, solvent exposure was not controlled in terms of the time of exposure or the amount of solvent used; the varnish was simply removed as in a normal cleaning procedure until no visible residue remained. It is recognised that a degree of variability will be involved in such a subjective procedure, although it was expected that the removal of varnish to the same endpoint would act as an internal control to some extent.

To test the degree of variability, five replicate tests of the same experiment were carried out, varnishing with B-72 in xylene, and cleaning with xylene. The levels of palmitic acid remaining in the paint films are plotted in Figure 3, as percentages of the initial levels, calculated from the untreated samples. Five paint samples were analysed at each stage (before varnishing, after varnishing and after cleaning) and mean values are plotted, with the degree of variation observed within each group of samples indicated. For comparison, results are included for samples of the same paint film immersed in xylene for 10 minutes and 24 hours.

Reductions in the level of palmitic acid in the paint films are observed after both varnishing and solvent cleaning, with reductions in the mean palmitic acid concentration (calculated from the GC analyses) of between 9 and 15% after varnishing alone, and between 12 and 17% after both varnishing and cleaning. Only small differences are seen between the results for the five samples, and these may be due as much to inhomogeneity in the paint film as to variations in experimental procedure. This result suggested that the procedure was reasonably reproducible, and duplicate tests only were carried out for the remainder of the varnish types.
Figure 3  Reductions in fatty acid levels in paint films after varnishing and cleaning treatments: replicates using B-72/xylene. (A) before treatment, (B) after varnishing only (cleaned mechanically), (C) after varnishing + cleaning (solvent cleaned). Results are included for 10 minute and 24 hour immersions in xylene.

Results obtained for the different varnish formulations are plotted in Figure 4. Data for Figures 3 and 4 are given in Table 2. The reductions in palmitic acid levels after varnishing correlate with the quantities found in the varnish samples, with extraction occurring in the order: dammar > MS2A > B-72 > Regalrez.

Further reductions after cleaning are not observed in all cases: the greatest difference is seen in the B-72 coated films cleaned with xylene, and for the other films the differences are smaller, in relation to the degree of variation found within the groups of samples. This is further evidence that the resin component of the varnish has a role in the leaching process.

5.4. Discussion

5.4.1. Influence of resin components

A consideration of the chemistry of the resin components of the varnishes provides a clearer explanation of the different effects observed. The chemistry of the synthetic, low molecular weight resins, Regalrez 1094 and MS2A, is not known precisely, but hypothetical structures, based on suppliers’ information and published studies [4-6], are given in Figures 5a and b. Regalrez 1094 is a hydro-
Extraction of soluble material from a paint film by a varnish solution

Table 2  Changes in palmitic acid levels in paint films after varnishing and cleaning treatments. Results for replicates of experiments are shown.

<table>
<thead>
<tr>
<th>Varnish</th>
<th>[P] b.t. 1</th>
<th>[P] a.v. 2</th>
<th>[P] a.c. 3</th>
<th>% a.v. 4</th>
<th>% a.c. 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraloid B-72 #1</td>
<td>17.1±1.1</td>
<td>15.1±0.6</td>
<td>14.2±0.7</td>
<td>88.4±3.6</td>
<td>83.1±3.9</td>
</tr>
<tr>
<td>Paraloid B-72 #2</td>
<td>16.1±0.8</td>
<td>14.6±0.2</td>
<td>13.5±0.5</td>
<td>90.7±1.2</td>
<td>84.0±2.9</td>
</tr>
<tr>
<td>Paraloid B-72 #3</td>
<td>15.7±0.4</td>
<td>13.3±0.6</td>
<td>13.3±0.5</td>
<td>84.7±4.0</td>
<td>84.2±3.1</td>
</tr>
<tr>
<td>Paraloid B-72 #4</td>
<td>16.6±1.2</td>
<td>15.0±0.7</td>
<td>14.5±0.2</td>
<td>90.5±4.1</td>
<td>87.4±1.5</td>
</tr>
<tr>
<td>Paraloid B-72 #5</td>
<td>16.4±0.5</td>
<td>14.8±0.4</td>
<td>13.9±0.7</td>
<td>90.3±2.3</td>
<td>85.1±4.3</td>
</tr>
<tr>
<td>Regalrez #1</td>
<td>15.9±0.6</td>
<td>14.5±0.4</td>
<td>14.7±0.8</td>
<td>91.0±2.5</td>
<td>92.7±5.2</td>
</tr>
<tr>
<td>Regalrez #2</td>
<td>13.2±0.8</td>
<td>12.1±0.7</td>
<td>12.3±0.4</td>
<td>92.1±5.3</td>
<td>93.0±2.8</td>
</tr>
<tr>
<td>MS2A #1</td>
<td>16.2±0.6</td>
<td>11.6±0.6</td>
<td>11.5±0.4</td>
<td>71.6±3.7</td>
<td>71.2±2.4</td>
</tr>
<tr>
<td>MS2A #2</td>
<td>15.7±1.0</td>
<td>10.7±0.7</td>
<td>10.6±0.7</td>
<td>68.4±4.1</td>
<td>67.2±4.5</td>
</tr>
<tr>
<td>Dammar 6</td>
<td>15.0±1.0</td>
<td>9.5±0.4</td>
<td>9.2±0.3</td>
<td>63.4±2.8</td>
<td>61.3±2.1</td>
</tr>
</tbody>
</table>

1. Palmitic acid concentration in paint film before treatment, expressed as μg per mg paint
2. Palmitic acid concentration after varnishing only (mechanically cleared)
3. Palmitic acid concentration after varnishing + cleaning (solvent cleaned)
4. % palmitic acid remaining in paint film after varnishing
5. % palmitic acid remaining in paint film after varnishing + cleaning
6. Only one experiment was carried out with dammar

Figure 4 Reductions in fatty acid levels in paint films after varnishing and cleaning treatments using different resins and solvents. (A) before treatment, (B) after varnishing only (cleaned mechanically), (C) after varnishing + cleaning (solvent cleaned).
carbon resin, made by oligomerisation of styrene and α-methylstyrene, and subsequent hydrogenation (Figure 5a). MS2A is a chemically reduced ketone resin. It is based on the same starting components as ketone resins: cyclohexanone and methyl cyclohexanone, but with the carbonyl groups replaced by hydroxyls (Figure 5b).

\[
\begin{align*}
a) & \quad R = H \text{ or } CH_3 \\
\text{Ethyl methacrylate} & \\
\text{Methyl acrylate} \\
b) & \quad R = H \text{ or } CH_3
\end{align*}
\]

**Figure 5** Typical chemical structures of resin components: (a) Regalrez 1094, (b) MS2A, (c) Paraloid B-72, (d) hydroxydammarenone, a component of dammar.

Paraloid B-72 is an acrylic resin, a copolymer of ethyl methacrylate (70%) and methyl acrylate (30%), represented in Figure 5c. The natural resin dammar has a complex composition, the major fraction consisting of triterpenoids: a diverse group of tetra- and pentacyclic hydrocarbons. One of the more abundant triterpenoids in dammar, hydroxydammarenone, is illustrated in Figure 5d. Numerous other structures have been identified, with variations in numbers and positions of hydroxyl, carbonyl and carboxylic acid substituents, and double bonds in the carbon skeleton [7-10].

The higher extraction values observed for MS2A and dammar seem most likely to be associated with the polar functionalities – hydroxyl, carbonyl and
carboxylic acid – contained in the structures of these resins. It is to be expected that the dissolution of a resin with polar character in a nonpolar solvent, such as the Sol340HT used in these experiments, will increase the overall polarity of the solution. The varnish solution can be considered in the same way as a mixture of solvents, with the solvent properties of the mixture being intermediate between those of the constituent solvents.

This influence of the resin component on the solvent properties of a varnish solution can also be illustrated by the solubility properties of mixtures of resins. Laropal A81 is a low molecular weight aldehyde resin, produced by condensation of aliphatic aldehydes with urea [11]. It is insoluble in low aromatic mineral spirits such as Sol340HT: when mixed with this solvent it softens and forms a discrete, gelled layer, but does not dissolve. When an equal amount of MS2A is added to the mixture, however, a clear solution of both resins in the solvent is formed. This is illustrated in Figure 6, which shows two mixtures made of 2g A81 in 10mL Sol340HT, with a further addition of 2g MS2A to the second mixture. The solvent properties of the Sol340HT have been modified by the addition of MS2A sufficiently to completely dissolve the A81.

Figure 6  Mixtures of resins with Sol340HT. A = 2g Laropal A81 + 10mL Sol340HT: a discrete, undissolved layer of the resin can be seen. B = 2g Laropal A81 + 2g MS2A + 10mL Sol340HT: the two resins form a clear solution.
5.4.2. Extraction of fatty acids

In terms of effects on the paint film, the greater quantities of fatty acids extracted by varnishes made with the more polar resins are consistent with the results of extraction with solvents, described in Chapter 4, with the more polar (aromatic or oxygenated) solvents having a greater leaching effect than nonpolar, hydrocarbon solvents. In contrast to MS2A and dammar, the hydrocarbon structure of Regalrez, with no polar substituents, produces a varnish solution with low polarity, explaining the low extraction values obtained for this resin.

The differences observed between palmitic acid levels in paint samples after varnishing alone (i.e. mechanically cleared), and after varnishing followed by solvent cleaning, shown in Figure 4, further illustrate this effect. For Regalrez and MS2A, extraction is seen to occur mainly at the varnishing stage, with the additional cleaning step appearing to have no significant effect. This supports the idea that it is the resin solution which is behaving as the active solvent in these cases, and a brief exposure to the free solvent, in cleaning, has no significant effect. (Although cleaning involves the production of a solution of the resin, this is immediately removed, and the paint film is predominantly exposed to the free solvent.) For the samples varnished with B-72, extraction of palmitic acid is seen to occur at both the varnishing and cleaning stages, indicating that exposure to the solvent, xylene, is sufficient to cause extraction, whether in a varnish or in its free form.

The quantities of azelaic acid extracted by the varnishes, shown in Figure 2, are also consistent with the previous solvent extraction results. Proportionally more azelaic acid is extracted by the MS2A and dammar varnishes, there were no detectable quantities of the acid in the Regalrez samples, and only minor amounts were detected in the B-72 samples.

5.5. Conclusions

The action of solvents on oil paint films is a consideration not only for cleaning treatments, but also for the application of a varnish, which involves exposure of the paint surface to solvent for a considerable period of time.

Measurements of the quantities of fatty acids extracted from an oil paint film by an applied varnish indicate that the effects of the varnish solution depend not only on the solvent used, but also on the resin component of the varnish. Varnishes formulated from resins with polar functionalities, represented in this study by the reduced ketone resin, MS2A, and the natural resin, dammar, were
observed to have a greater leaching potential than a varnish formulated from the hydrocarbon resin, Regalrez 1094, in the same solvent.

Practical situations in which these effects could be a particular consideration include the varnishing of a painting which shows vulnerability to solvents, in which case the choice of a hydrocarbon resin may be more appropriate than an oxygenated resin, such as the MS2A and dammar tested here. If repeated applications of a working varnish are being made to a painting during treatment, it would also be preferable to use a nonpolar, hydrocarbon resin.

The influence of the resin component on the solvent properties of a varnish solution also helps to explain some phenomena observed in conservation treatments, such as the disruption of inpainting by a subsequent varnish application, where the solvent used in the varnish on its own would not be expected to dissolve the inpainting medium. For example, the application of a final varnish of MS2A, in a mineral spirit solvent such as the Sol340HT used in these experiments, has been found to disrupt (i.e. resolubilise) inpainting applied in Laropal A81, whereas a final varnish of Regalrez in the same solvent has no effect on the inpainting [12].

The results obtained for the paint film in this study are deliberately exaggerated, and will not be directly applicable to the wide range of paint films encountered in practice. As illustrated in previous chapters, the response of a painting to different treatments will depend on its exact chemical composition, which will vary greatly according to factors such as its age and the materials used. The different effects observed in these experiments, however, demonstrate that the resin component of a varnish should be taken into account, in addition to the solvent used for its application, when considering possible solvent effects on a painting.

Materials

Paraloid B-72 (formerly Acryloid B-72): Conservation Materials Ltd., 1165 Marietta Way, P.O. Box 2884, Sparks, NV 89431, USA, (702) 331 0582.

MS2A: Linden Chemicals Ltd., 18 Trinity Court, Birchwood, Warrington, Cheshire WA3 6QT, UK, (0925) 850220.

Regalrez 1094: Hercules Inc, 1313 North Market Street, Wilmington, DE 19894, USA, (302) 594 5000.

Dammar, Shell Sol340HT: Conservation Support Systems, 924 West Pedregosa Street, Santa Barbara, CA 93101, USA, (805) 682 9843.
References


