Solvent extractable components of oil paint films
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2. A review of studies of solvent action

Abstract

This chapter presents an overview of research which has been carried out into the effects of organic solvents on oil paint films, including a brief survey of related studies concerned with alternative (gelled/aqueous) cleaning systems and paint media other than oil. The relative advantages of studies based on model paint films, and those carried out using paintings, are discussed, and an outline is given of material presented in subsequent chapters.

2.1. Introduction

During the Select Committee Enquiry which followed the first cleaning controversy at London's National Gallery, Charles Eastlake, who was Keeper of the Gallery at the onset of the controversy in 1846, was questioned on the value of scientific research into conservation issues. The questions related to statements by Michael Faraday, who had, at the request of the Committee, carried out some simple experiments of his own on the removability of varnish from several paintings, and had suggested that further research on issues such as cleaning would be useful [1, pp. 373-383].

While Eastlake agreed that "it would be desirable to have the assistance or advice of chemists, with reference to the restoration of pictures", he believed that scientists should be consulted rather than employed at the Gallery, stating that it would "complicate the machinery very much" if the Government decided to "appoint chemists to consider how solvents and chemical applications act upon pictures" [1, p. 469]. His remarks are of historical interest since, had his attitude been different, research into cleaning and solvent effects might have been taking place at the Gallery almost a century earlier than Graham's investigations in the 1950s [2, p. 184].
Although the majority of research on the subject has been carried out subsequent to this date, a number of studies had been carried out previously, and some of the research in the industrial field dealt with related issues. This chapter will summarise research to date into solvent effects on oil paint films, with some reference to studies on related subjects, such as solvent effects on other paint media, and the use of aqueous/gelled cleaning agents. Research has tended to focus on the use of volatile solvents, and their effects on oil paint, since these are, respectively, the most widely used cleaning agents, and the most commonly used medium in traditional painting techniques. In addition, oil is a very versatile medium which is associated with a wide range of methods of application, including fine surface applications – glazes, scumbles, etc. – which has contributed to the popular perception of oil paintings being particularly sensitive to solvent cleaning, as was shown in the previous chapter. This has also made it an obvious focus for research into solvent effects.

The mechanisms and techniques of varnish removal, which have also been the subject of a number of studies, will not be addressed here, except where results pertain to effects on paint films.

### 2.2. Early studies

In the early part of the twentieth century, there were numerous studies in industry of the properties and behaviour of drying oils such as linseed oil, because of the importance of these materials in coatings applications. Although more attention was paid in these to the effects of outdoor exposure conditions such as water and prolonged UV irradiation than to the effects of organic solvents, some of the earlier investigations used solvent extraction of oil films as a means of elucidating the drying mechanisms of the oil.

Morrell in 1915 described acetone soluble fractions of linseed and poppy-seed oil polymerised at high temperature [3], and similar measurements were later made by Elm, using trilinolenin as the film-forming material, and extracting dried films in acetone, benzene and carbon tetrachloride [4]. The extractable material in these studies corresponded to the fraction of the oil not yet polymerised into the solidified network, and was shown to become diminished during the initial drying process: Nelson carried out stress-strain measurements on paint films, including linseed oil, and interpreted these in terms of solid and liquid phases in the films, with loss of elasticity resulting from a reduction of the liquid phase in the early stages of drying and oxidation [5]. Experiments by Long and co-workers supported this idea, with a reduction in the proportion of acetone soluble phase in trilinolenin films observed over a year of drying [6]. In addition, the dried films in this study
were extracted in a range of solvents, and greater proportions of material were found to be extracted by oxygenated solvents, relative to hydrocarbons. Payne demonstrated the influence of factors such as thickening pretreatments and the use of driers on the amount of solvent extractable material in linseed oil films dried for 3 or 6 weeks, using acetone, methanol and benzene [7].

The first systematic studies of solvent effects in relation to cleaning paintings were carried out by Stout in the 1930s. His experiments were designed to investigate the mechanism of varnish removal, using a combination of solvent exposure and mild friction, but since his series of "varnishes" included linseed oil, some general observations could be made regarding potential effects on oil paint films [8]. A small percentage (3-4% by weight) of film material was found to be removed from seven month old films of linseed oil by brief exposure to acetone, ethanol or ethylene dichloride, presumably from a combination of leaching and abrasion of the softened film. Naphtha and toluene had no measurable effect.

At around the same time, Laurie described simple, empirical tests demonstrating the softening effects of vapours of a series of solvents on the paint layers of a forty year old painting, although details of the paint composition and solvent exposure were not provided [9].

Graham's experiments, like Stout's, were designed to investigate varnish removal, although he too examined linseed oil and interpreted the results in terms of potential effects on paint layers [10]. Solvent was observed to diffuse into and swell oil films, with a sharp boundary between the swollen and unswollen material. Different solvents were found to diffuse at different rates, in some cases relating to the viscosity of the solvent. Leaching was measured (40-44% by weight of 6 month old films extractable in ethanol, acetone and benzene) and the potential for embrittlement of paint films as a result of loss of this plasticising, soluble material was cautiously noted.

Swelling of oil films – calculated from dimensional changes of detached samples in solvent – was measured for a variety of solvents, with the most significant observations being made for solvent mixtures. The swelling effect of certain binary mixtures was found to be greater than that expected, assuming a linear relationship between the fractional composition of the solvents and the degree of swelling, as illustrated in Figure 1. This finding cast doubt on the then common practice of using restrainers in cleaning – in which an "inactive" solvent such as turpentine is used to dampen the cleaning action of an "active" solvent such as ethanol – since the swelling action of the resultant solvent mixture may actually be greater than either of the solvents alone. This phenomenon will be discussed in more detail presently.
Chapter 2

Figure 1 *Equilibrium swelling of linseed stand oil film in binary solvent mixtures: generalised diagram representing mixtures of turpentine with a polar solvent such as acetone or ethanol (reproduced from Graham [10]).*

Further observations on swelling and leaching of pigmented and unpigmented linseed oil films, in organic solvents and water, were made by Browne [11], although these were oriented to outdoor coating applications (some of the films were “weathered” by UV irradiation and spraying with water). Paint films were generally found to have an increased density after solvent exposure and drying, and some of the films also became porous after solvent treatment. Swelling was measured using a travelling microscope, and the results were interpreted in terms of polarity of paint films and solvents: for example, certain pigments (titanium and zinc oxides) caused increased swelling of paint films in water relative to the organic solvents, and Browne suggested this was a consequence of the more hydrophilic nature of paints made with these pigments.

2.3. *Swelling and leaching described in detail*

The investigations by Stolow in the 1950s-70s built substantially on the concepts identified by Stout and Graham, providing detailed descriptions of swelling and leaching phenomena, and explaining some of the important factors determining the response of paint films to solvent [12-15].

Stolow made precise measurements of vertical swelling of supported paint films using a specially designed instrument, in which solvent was supplied to the paint film from a flat-ended tube positioned very close to the paint surface, and
A review of studies of solvent action

Variation in solvent flow was used to indicate dimensional changes in the film [16]. Using this technique, the processes of swelling and leaching were followed for a variety of unpigmented and lead white pigmented films, up to 25 years old: swelling was found to reach a maximum within a few minutes (depending on factors such as paint film thickness and the solvent used), after which a degree of shrinkage occurred, corresponding to the continued leaching of soluble material from the film. After drying, the solvent treated films were found to be denser and more compact, in common with Browne’s findings, as well as more brittle. The same paint films exposed to solvent for a second time exhibited predominantly swelling behaviour, gradually increasing to an equilibrium value, and without any observable shrinkage from leaching [15, pp. 55-62]. The typical pattern of swelling and leaching is illustrated in Figure 2.

![Swelling graph](image)

**Figure 2** Swelling of 7 year old stand oil film in acetone, showing swelling and leaching of the “virgin” film (a), and re-swelling of the same, leached film (b) (reproduced from Stolow [14]).

The equilibrium swelling values for a range of solvents were interpreted in terms of molecular volumes and, more importantly, solubility parameters. Swelling values for lead white pigmented stand oil films up to 14 years old were plotted in order of solubility parameters of the solvents used, using the system of Hildebrand [17, pp. 424-439], and maximum swelling was found to correspond roughly to the solubility parameter region 9.3-9.9. This region includes methyl ethyl ketone,
cyclohexanone and a number of chlorinated solvents (an observation which accounts for the use of methylene chloride as a common ingredient in commercial paint strippers [18]). Solvents far removed from this region – with solubility parameters under 8 (various mineral spirits and hydrocarbons) or over 13 (methanol, water) – caused very little swelling. Although absolute swelling values varied according to the age of the paint film, the pattern, and the “peak” swelling region, were the same [15, pp. 90-95]. Results for two paint films, aged 27 weeks and 7 years, are shown in Figure 3, with the corresponding Hildebrand parameters in Table 1.

**Figure 3**  *Equilibrium swelling of lead white stand oil films in solvents, plotted in order of Hildebrand solubility parameters, for films aged: a) 27 weeks; b) 7 years (reproduced from Stolow [14]).*

This treatment of the data helped to explain Graham’s results from binary solvent mixtures: a mixture of two solvents with solubility parameters on either side of the swelling region, such as turpentine and ethanol, may have a greater swelling effect than either of the pure solvents, since the solubility parameter of the mixture will be intermediate between those of the individual solvents. If both solvents are on the same side of the swelling region, however – as Graham observed for benzene/chloroform and acetone/water mixtures – this effect will not be observed. Stolow examined a number of solvent mixtures in this way [13, pp. 400-401]. He also suggested that, using his data, a solvent’s swelling properties could be predicted from its solubility parameter. This concept was later developed...
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Table 1  Hildebrand solubility parameters ($\delta$) for solvents in Figure 3 (from Stolow [13, 15]).

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\delta$</th>
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<tr>
<td>1 isooctane</td>
<td>7.3</td>
<td>15 trichloroethylene</td>
<td>9.3</td>
</tr>
<tr>
<td>2 $n$-hexane</td>
<td>7.3</td>
<td>16 ethylene dichloride</td>
<td>9.8</td>
</tr>
<tr>
<td>3 $n$-heptane</td>
<td>7.4</td>
<td>17 cellosolve 1</td>
<td>9.9</td>
</tr>
<tr>
<td>4 white spirit</td>
<td>7.6</td>
<td>18 cyclohexanone</td>
<td>9.9</td>
</tr>
<tr>
<td>5 cyclohexane</td>
<td>8.2</td>
<td>19 acetone</td>
<td>10.0</td>
</tr>
<tr>
<td>6 turpentine</td>
<td>8.5</td>
<td>20 methyl cellosolve 2</td>
<td>10.8</td>
</tr>
<tr>
<td>7 carbon tetrachloride</td>
<td>8.6</td>
<td>21 sec-butyl alcohol</td>
<td>10.8</td>
</tr>
<tr>
<td>8 ethyl benzene</td>
<td>8.8</td>
<td>22 $n$-amyl alcohol</td>
<td>10.9</td>
</tr>
<tr>
<td>9 xylenes</td>
<td>8.8</td>
<td>23 isobutyl alcohol</td>
<td>11.1</td>
</tr>
<tr>
<td>10 toluene</td>
<td>8.9</td>
<td>24 $n$-butyl alcohol</td>
<td>11.4</td>
</tr>
<tr>
<td>11 methyl-$n$-propyl ketone</td>
<td>8.9</td>
<td>25 isopropyl alcohol</td>
<td>11.5</td>
</tr>
<tr>
<td>12 benzene</td>
<td>9.2</td>
<td>26 $n$-propyl alcohol</td>
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<td>13 diacette alcohol</td>
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<td>27 ethanol</td>
<td>12.7</td>
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<tr>
<td>14 methyl ethyl ketone</td>
<td>9.3</td>
<td>28 methanol</td>
<td>14.5</td>
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1 2-ethoxyethanol
2 2-methoxyethanol

in more practical terms by Hedley, who used Stolow's data in combination with the system of Teas for graphically presenting solubility data [19] to predict solvent mixtures for cleaning which would minimise potential risks to the paint layers [20]. This adaptation of the solubility parameter data to a simple, triangular plot has proved to be a useful visual aid in the selection of cleaning solvents. Hedley also used this approach to rationalise certain applications of the “safety margin test” for cleaning, which had been proposed by Ruhemann as a simple, empirical precaution, but which, in the general form he presented, had the drawback of assuming a more linear relationship between the concentration of “active” solvent in a mixture and its swelling/solubility properties [21, pp. 192, 308-313]. As illustrated in Figure 1, such linearity is not always followed, and the concept of “diluting” an active solvent can be misleading.

The swelling data was further interpreted by Stolow in terms of diffusion rates of the different solvents, by comparing the times taken for swelling to reach completion [15, pp. 95-105]. Solvents exhibited trends according to their molecular volume and viscosity: those of low viscosity, such as acetone and benzene, produced much more rapid swelling than more viscous solvents such as isobutyl alcohol. Solvents with low molecular volume, such as methanol, also showed rapid diffusion and swelling. In addition, diffusion rates were dependent on film
properties, with swelling occurring more rapidly in thin films, and more slowly in pigmented as compared to unpigmented films. De-swelling — corresponding to evaporation of solvent from the paint film — was studied in some cases, and was found to occur more slowly than swelling. Unsupported paint samples exhibited more rapid swelling than supported films, as a result of the greater surface area available for solvent penetration [15, p. 56].

As a complement to his studies of swelling, Stolow investigated the process of leaching in some detail, using a wider variety of linseed oil paint samples [15, pp. 62-68]. The majority of these were laboratory-prepared films, aged from <1 to 25 years, with some exposed to additional light or thermal accelerated ageing conditions. For lead white pigmented films and unpigmented films of stand oil and alkali refined linseed oil, the maximum amount of leaching was generally found to be between 15 and 30% of medium content by weight for the range of films and solvents tested. With the exception of n-hexane, the leaching effects of the solvents tested — which included alcohols, ketones and chlorinated solvents — were found to be of the same order. The relatively low leaching effect of n-hexane was attributed to the low swelling power of this solvent. Experiments using different times of exposure to solvent indicated that leaching initially occurred rapidly, with 50% of the total soluble material extracted from lead white pigmented and unpigmented films in acetone within 100 seconds, although the process was slow to reach completion, taking over 3 days in some cases.

Higher leaching values were found for oil films made with other pigments: between 46 and 56% of medium was extracted from films pigmented with barium sulphate using various solvents, and as much as 84-87% was extracted from titanium dioxide and iron oxide pigmented films in acetone. These more pronounced values reflect a physical disintegration of the paint samples in solvent, a consequence of the pigments having a photocatalytic effect on the degradation of the oil polymer, accelerated in these cases by UV ageing.

Quantities of extractable material showed some relationship with age of the paint film, with paint films studied over a period of 25 years showing an initial decrease in the proportion of material extractable, followed by a gradual increase. This was explained in terms of the different reactions occurring in the film: it was suggested that an initial rapid polymerisation results in a reduced quantity of extractable material, as demonstrated in earlier studies, but that after longer periods of ageing, progressive oxidative degradation produces increasing quantities of extractables. Unpigmented films in particular showed a pronounced increase in quantities of extractable material after longer ageing periods, up to 15 years. This trend was not borne out by preliminary analyses of older paint samples, however (examples were from a 48 year old palette, and a 17th century painting). These
gave leaching values of the same order as, or lower than, those for the younger paint films [15, pp. 65, 85].

Stolow analysed the solvent extracts from various paint films, using gas chromatography and infrared spectroscopy, to determine their composition. These results will be discussed in the following chapter, which will describe the relationship between the drying reactions in the oil and the nature of the solvent extractable components.

On a practical note, both Graham and Stolow suggested the possibility of re-plasticising, or “nourishing” paint films, using some kind of nonvolatile, non-drying substance to replace the material removed by leaching [10, p. 504; 14, p. 88]. This was not a new idea: the rejuvenation of a picture’s surface after cleaning by the application of some kind of oil (drying or non-drying) was not uncommon in the past, although presumably it was carried out more for aesthetic than for mechanical purposes. Such treatments have never been generally accepted, however: although a number of nineteenth century manuals recommended the practice, one commentary includes a reference to the use of olive oil to “restore the oil in the paint which it was supposed had dried out of it”, and condemns “this most pernicious process ... than which nothing can be more injurious” (although the supposedly injurious effects are not specified) [22, pp. 613-614]. The obvious problem with the use of a drying oil for this purpose would be the likely irreversibility of the process, but the idea of applying this kind of treatment with alternative materials in a more scientific, controlled manner has not received much attention. This is perhaps because it is felt to go against the general principle of minimal intervention in conservation: since the visual problems of surface mattness attributed to leaching can be largely resolved at the varnishing stage, such a “nourishing” treatment would be intended primarily to improve the paint layer’s long term physical stability, and it would be very difficult to judge the need for this kind of treatment in any particular case, or indeed its success. Hence it would be difficult to justify what would be a relatively invasive treatment, unless the paint was in obviously poor physical condition, in which case a more conventional consolidation treatment would generally be appropriate.

2.4. Later studies

Studies subsequent to Stolow’s have provided additional information on swelling and leaching effects, which in a large part corroborates the previous research. Jones used one year old, unpigmented stand and raw linseed oil films in his studies, and found approximately 16 and 38% of these films to be extractable
by weight, respectively, in isopropanol. Increased quantities of extractable material were found for UV irradiated films, and from this Jones postulated that oil paint films would generally show increasing quantities of soluble material with age, corresponding to a progressive deterioration of the binding medium [23].

The embrittlement and increased density of paint films as a consequence of solvent leaching were measured in a study by McGlinchey, using differential scanning calorimetry [24]. He analysed films of poppy, walnut and linseed oil pigmented with titanium, lead and zinc white pigments, which had undergone accelerated ageing treatments, and found the polar solvents acetone and ethanol to have a greater effect than cyclohexane, which caused no observable changes in the paint films' physical properties. The effects of solvents on mechanical properties of paint films were also investigated by Hedley and co-workers, who used thermal mechanical and dielectric analysis techniques to analyse 12 year old oil films pigmented with lead white and burnt sienna [25]. Increased stiffness was observed as a result of exposure to acetone and isopropanol, which again was attributed to the leaching out of soluble components, although water was found to cause a reduced stiffness. Changes were found to result from swab rolling with solvents, as well as from immersion in solvent, although the effects of swabbing were less pronounced. Surface changes were also investigated in this study using scanning electron microscopy (SEM), with erosion observed in some samples as a consequence of loss of organic binder. Solvent effects were less in the lead white samples, as compared to the burnt sienna, with respect to both stiffness and surface changes. This can be attributed to the lower medium content of the lead white paint, as well as the different drying properties of the pigments.

More recently, similar results were obtained by Tumosa and co-workers [26], who made stress-strain measurements on oil paint films made with various pigments, aged between 6 and 20 years. Increased brittleness and stiffness were observed after exposure to acetone or toluene for as little as 30 seconds. Samples tested before the solvent had completely evaporated showed a reduced stiffness in some cases, demonstrating the softening effect of the retained solvent. The results of this study were interpreted, a little speculatively, in terms of a painting's ability to tolerate stresses from environmental fluctuations and handling following solvent treatment, on the basis that the solvent exposed films in the tests retained a degree of elasticity and plasticity.

Erhardt and Tsang [27] compared solvent effects on a range of pigmented oil paint films, aged between 5 and 50 years. Solvent extraction was measured in terms of both weight changes and quantities of palmitic acid in the extracts, determined by gas chromatography (the analysis of leachable components by GC and GC/MS in this study will be described more fully in the following chapter).
Results were generally in agreement with Stolow's data, with the aromatic and oxygenated solvents: toluene, acetone and ethanol, producing higher leaching values, and hexane having a lesser effect. Pigmentation was shown to have a pronounced effect on the quantities of material extractable, with the greatest proportions extracted from raw sienna films, and the least from lead white films. This difference was attributed in this case to the greater extent of cross linking in the latter, catalysed by the lead white pigment. No clear correlations were observed between the age of the paint films and solvent effects. In addition to leaching of organic material, pigment was reported to be lost as a result of solvent treatment in many cases, presumably more from films made with the poorer drying pigments such as raw sienna, indicating the pronounced solvent sensitivity of some of the samples used.

Different exposure times to solvent were used, including a few measurements of quantities of fatty acids extracted by swabs, but these data were not compared with the immersion results. Changes in gloss were also measured, and in general these paint films showed the reduction in gloss after solvent exposure that would be expected, as a result of surface erosion from leaching, as well as from pigment loss in some cases.

The same authors published additional data [28], in which leaching values for a variety of solvents were interpreted in terms of solubility parameters. Lead white and raw sienna films were found to differ only in the overall quantities of material extractable, not in their relative responses to different solvents. It was suggested from this that the response of these paint films was not related to differences in the extent of oxidation in the oil polymer, which might be expected to shift the solvent sensitivity towards more polar solvents, but to other factors such as the overall degree of polymerisation.

The same paper described experiments demonstrating that the application of a solvent based varnish to an oil paint film 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 GC, 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. This idea will be addressed in more detail in Chapter 5.

The quantities of fatty acids extractable from paint films made with a variety of oil types, using four solvents, have been measured in a recent study by Schilling and co-workers [29]. This was done primarily to investigate potential changes in fatty acid ratios which might influence medium analyses: significant proportions of fatty acids were extracted from the films tested, but this did not hinder identification of the oil type.
Solvent retention in paint layers was measured by Dauchot-Dehon, using radio-isotopically labelled solvents applied to fragments of an 80 year old painting [30]. Results were consistent with previous studies of solvent loss from polymers [31], demonstrating a two stage process: an initial, rapid loss corresponding to evaporation from the paint surface; and a slower loss of residual solvent, limited by diffusion through the paint structure. The second stage was very slow to reach completion, with measurable quantities of solvent retained for long periods, over a month in some cases.

A related study by Masschelein-Kleiner and Deneyer used gravimetric measurements to follow solvent loss from similar paint samples [32]. A wide range of solvents were classified according to the time taken to evaporate from the samples, and also to their rates of penetration, which were based theoretically on measurements of viscosity and surface tension. Solvent mixtures for cleaning were recommended by the authors, on the principle that those with strong penetration and retention are the most dangerous to the paint layers. Such specific recommendations are potentially misleading, since they fail to acknowledge other important factors – most obviously, solubility parameters and associated swelling effects. Solvents not retained strongly in the paint samples in these experiments included a number of chlorinated solvents identified in other studies as strong swellers of oil paint, for example, and Hildebrand parameters for some of the recommended mixtures actually fall in the peak swelling region identified by Stolow [15]. Another problem is that the criteria of penetration and retention do not discriminate neutral solvents from acidic and basic compounds – ammonia and formic acid are included in some of the proposed cleaning mixtures, and the distinct risks associated with these materials are not referred to in the study.

The conflicting recommendations from different studies illustrate the complexity of the problem of determining risks in solvent cleaning, and the numerous parameters involved. Diffusion and evaporation are indeed important factors – one of Ruhemann’s criticisms of Stolow’s research, with reference to the use of acetone for cleaning, was that his immersion and swelling data downplayed the contribution of these properties [21, p. 201]. As Ruhemann correctly observed, much of the safety of cleaning relies on careful manipulation of solvents by the conservator: scientific studies necessarily use simplified models of cleaning, which in most cases can only provide general indicators of risk. Any specific recommendations of cleaning solvents based on scientific studies, such as those of Masschelein-Kleiner and Deneyer, must be carefully qualified, otherwise there is a risk of creating a false sense of security in their use.

Michalski expressed similar reservations about practical interpretations of scientific data in his 1990 review of cleaning research, commenting that “the
subject requires more data and critical study from experienced practitioners before specific recommendations make sense" [33, p. 85]. His summary concentrated on the physical aspects of solvent action, including diffusion and evaporation, but also taking into account factors such as capillarity, occurring through cracks or pores in the paint structure, and the influence of pigment particles. The disruption of pigment-medium interfaces by solvent interactions with pigment particles was proposed as a possible cause of blanching, independent of any effects of leaching or surface erosion. This theory might account for some instances in which a paint area is very difficult to saturate with varnish, since such light-scattering voids within the paint layer, around pigment particles, would generally be inaccessible to varnish applied to the paint surface.

Michalski also re-interpreted swelling data from previous studies using a three dimensional plot of solubility parameters, which, although less visually comprehensible than the Teas plot used by Hedley, described above, allowed for a more accurate distinction between different solvent properties.

The problems of successfully applying solubility parameter systems to cleaning problems have been discussed by Phenix [34], who pointed out that such applications are constrained not only by the limitations of the systems themselves in describing solvent properties, but also by the limited available data on solubility properties of aged painting materials – varnish and, more importantly, oil paint. He suggested that the interpretations based on Stolow’s swelling data, most of which were obtained on relatively young films made with stand oil, may underestimate the importance of polar interactions – hydrogen bonding in particular – which might be expected to be more significant in aged paint films that have undergone a greater degree of hydrolysis and oxidation. In practical terms, this would result in a shift of the swelling region for oil paint towards the more polar area of, for example, the Teas chart. With regard to the solubility parameter systems themselves, Phenix described more up to date systems, which give a better discrimination of factors such as hydrogen bonding, and presented these as possible alternatives to the systems adapted by Hedley and Michalski.

In a separate paper, Phenix reported on the use of a system of microscopy combined with digital image analysis to provide accurate measurements of dimensional changes in paint samples immersed in solvent [35]. This is one of the few published studies of swelling effects since those of Stolow, along with the work of Eissler and Princen, who made measurements of tensile and swelling properties of pigmented and unpigmented linseed oil films in various solvents [36]. Their results correlated fairly well with Stolow’s data, although more attention was paid to the effects of water than to organic solvents. Initial results described by Phenix, obtained on thermally aged umber/oil paint samples, also showed some of the same trends as in the swelling data of Stolow, in terms of solvent properties.
such as diffusion coefficients and solubility parameters. Some of the more polar solvents, ethanol and methanol in particular, caused greater swelling than had been found by Stolow, however. Basic reagents, triethanolamine and ammonium hydroxide, were also tested, and exhibited strong swelling properties. A small number of older paint samples were tested, from eighteenth and nineteenth century paintings, and these showed very little swelling in acetone (approx. 1-2% change in area). A decrease in equilibrium swelling values of paint films aged up to 25 years in certain solvents had been observed by Stolow [15, p. 93], and these initial results on much older paint samples suggest that this reduction in swelling potential may be an ongoing trend.

2.5. Studies of other paint media and cleaning systems

Since the effects of volatile organic solvents on oil paint films are the focus of this thesis, research into alternative paint media and cleaning agents will only be briefly summarised here.

The response of egg tempera paint films to solvents were investigated by Khandekar and co-workers [37], using films prepared with various pigments and exposed to light and thermal ageing regimes. Surface changes as a result of solvent immersion or swabbing were monitored using SEM, and quantities of lipid material extracted were determined using GC. Significant quantities of the lipid content of these films were found to be extractable using organic solvents, particularly chlorinated solvents. Solvent extractable components of “megilp” paint samples (made using combinations of drying oil and mastic) were analysed by Kokkorii and colleagues, using direct temperature-resolved mass spectrometry (DTMS) and GCMS [38]. Not surprisingly, considering the notorious solvent vulnerability of this type of paint medium, large proportions of the megilp samples were solvent extractable, particularly in the polar solvents ethanol and acetone. Soluble compounds were derived from both the resin and oil components of the megilps. Boon and Van Och described the use of mass spectrometric techniques to investigate the effects of different cleaning treatments on a solvent sensitive wax-oil painting, and found that a rapid method of varnish removal using a polar solvent mixture minimised the extraction of wax components from the paint layers [39].

Burnstock and Learner studied the cleaning action of a range of alkaline cleaning reagents, including aqueous solutions, wax pastes and soap gels [40]. This study was concerned primarily with the effectiveness and mechanisms of removal of an aged mastic varnish from an oil primed canvas, but some observations were made on the effects of cleaning agents on the oil priming: erosion of the priming
layer was observed in some cases using SEM, particularly with cleaning formulations of high pH. This is consistent with the alkaline hydrolysis of the oil medium which would be expected from the use of such basic reagents.

The past decade or so has seen a considerable amount of research concerned with the aqueous and gelled cleaning formulations developed by Wolbers [41]. These were designed to introduce a greater degree of control and specificity to the cleaning process, with various gels and emulsions formulated to act selectively on individual varnish or overpaint layers. Recipes are based on resin acids (structurally similar to natural varnish resins), enzymes or more traditional solvents as active ingredients.

One of the theoretical advantages of these systems is the limited penetration of solvents into the paint layers, with a consequently reduced risk of associated swelling and leaching effects. This assumption has been tested by a number of studies, including a simple investigation by Southall, who incorporated coloured dyes into gel and emulsion mixtures in order to empirically measure the extent of absorption and dispersion of the solvent components into a number of painted substrates [42], and found that capillary absorption was not significantly limited in all cases. Another study included GC analyses to quantify fatty acids extracted from a test paint film by immersion in an ethanol gel, which indicated that similar quantities of material were extracted from the paint by exposure to the gelled solvent as by exposure to liquid ethanol for the same period of time, and more than by other solvents such as hexane and toluene [28]. Gels made with abietic acid and triethanolamine (TEA, an organic base included in resin based cleaning formulations for the formation of the resin acid salts) were also found to cause leaching of fatty acids, in comparable quantities to free solvents. A later study by Erhardt and Bischoff also found gels formulated with TEA to be active in extracting fatty acids from test paint samples [43].

Koller carried out experiments in conjunction with the cleaning of a nineteenth century painting using a gel based on deoxycholic acid [44], and concluded that this bile acid was more effective in removing oil components from the varnish than in its intended purpose of dissolving the oxidised resin. This observation had obvious implications for the potential effects of deoxycholic acid on oil paint layers, and a subsequent study by Ford and Byrne tested this idea, measuring the relative effects of swab applications of a number of solvents and gel formulations, in terms of extraction of fatty acids from paint layers during cleaning [45]. Two paintings were used in the tests, approximately 90 and 3 years old, and although fatty acids were detected in swabs with both solvents and gels, no evidence was found for the preferential extraction of lipid components by resin soap gels, as might be expected from Koller’s results.
Another important concern with the use of gels and emulsions is the clearance of the nonvolatile components – including detergents, gelling agents and organic bases – from the paint surface after cleaning. The retention of such components has been studied, using radio-isotopically labelled compounds [46, 47] and by GCMS analysis of varnish or paint samples after cleaning [44, 48, 49], and appreciable residues of detergents and resins have been detected on treated surfaces, even after recommended clearance procedures. Effective clearance was more of a problem for cleaning mixtures of high pH and detergent concentration [46]. Residue are a particular concern for compounds which might be expected to show chemical activity in the long term, a problem which has been postulated for the surfactants Triton X-100 [48] and Ethomeen C-12 [50], as well as for TEA [43, pp. 19-20]. In addition, TEA has been found to have a softening effect on test paint films [26].

Researchers and conservators have also questioned the roles of different ingredients in the cleaning mixtures, with some studies indicating that the supposedly active components – resin acids [48, 51] or lipase enzyme [52] – contribute less to cleaning activity than the other components, intended primarily as emulsifiers, counterions for resin acids, or buffers.

Despite the problems associated with these cleaning systems, successful applications have been reported for problematic cleaning treatments in which conventional solvents were not found to give sufficient control or selectivity [41, 53, 54]. It has generally been stressed though that gels and emulsions are not intended as replacements for traditional solvent cleaning methods, but as additional tools to enable conservators to address a wider range of cleaning problems [53, p. 130; 55, p. 75].

2.6. Model studies versus experiments on paintings

The majority of the studies described above have been carried out using laboratory-prepared paint films rather than samples from paintings, the main reason being, as Stolow observed, “it is preferable to obtain data on films of precisely known composition and origin, than to experiment on films whose past history is uncertain.” [12, p. 10]. Aside from practical limitations, there are also obvious ethical constraints on the extent to which experiments can be carried out on old paintings, unless fragments of paintings are available for test purposes (several of the studies described used such fragments as test material). Laboratory prepared films have the additional advantage that they can be formulated with a variety of pigments, media, film thicknesses, etc., to investigate the influence of these factors in a controlled manner. However, model paint films are necessarily
much younger than the paint layers they are intended to represent, and the extent to which data from model studies can be related to solvent effects on paintings has been much debated, as was illustrated in the previous chapter. Exchanges on the subject have sometimes become quite fervent [56].

The concern is a valid one. The long term drying chemistry of oil paint is not thoroughly understood, but it is recognised that paint films continue to undergo chemical and physical changes over long periods of time, as has been highlighted in recent research [57]. Paint films of considerable age, as in paintings hundreds of years old, are therefore likely to show differences in their response to solvents from the younger, model paint films. Some studies have used accelerated ageing treatments in an attempt to produce paint films closer in character to significantly aged films, but for a chemically complex system such as drying oil, particularly if pigment is present, doubt has been expressed as to whether conditions of intense light and/or elevated temperature can be used to accurately reproduce the same combinations of reactions that occur during long term, ambient ageing [58, p. 598; 59].

A novel approach to cleaning research was taken in a recent study by White and Roy, which was the first to present comparative analyses of samples taken from a series of paintings, dating from the fifteenth to nineteenth centuries, in the course of cleaning treatments [60]. (Other researchers have used samples from paintings to investigate cleaning effects [39], but this was the first systematic and extensive study of traditional oil and tempera paintings.) Paired samples were analysed from paint areas cleaned mechanically (representing the paint film “before cleaning”), and using solvents, and no general differences were observed between the samples, either in their organic composition (studied by GCMS) or physical structure (porosity, studied by SEM). One limitation of the organic analysis was that, at least in the form published, the interpretations were only semi-quantitative, relying on visual comparisons of chromatograms, from which it was difficult to judge what were stated to be “negligible” or “insignificant” differences. Quantitative data, such as peak area ratios, would have allowed for more critical comparisons. The SEM comparisons were more persuasive, and made more sense in this respect, since the textural features of a paint layer are far more difficult to quantify. Some quantitative GCMS data were presented, on extracts obtained from swabs after gently rubbing over exposed paint surfaces, and these were more convincing than the whole paint analyses, with only trace quantities of fatty acids detected in these cases, even after prolonged exposure to acetone or propanol. Analytical aspects of this study will be discussed in more detail in Chapter 6, which describes experiments based on a similar approach of analysing samples from paintings before and after cleaning.
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This research was important in that it began to put the model studies in a practical context, and provided data to support the generally held suspicion that cleaning effects on significantly aged paint layers are considerably less pronounced than the effects observed in studies of test films under more extreme conditions. Such model studies were perhaps too readily dismissed by the authors, however, and some of the statements about cleaning over-generalised – such as a reference to "the long-held assumption of the safety and reliability of solvent cleaning methods for old master paintings" [60, p. 160], neglecting to acknowledge the fact that many paintings are certainly vulnerable to damage by solvents, as discussed in the previous chapter.

2.7. Aims of the current study

The data of White and Roy demonstrate the problems in extrapolating data from the study of model paint films to represent the behaviour of much older films. Nonetheless, the study of model films is important as it allows systematic, quantitative studies which are difficult or inappropriate for old paintings, for which – as mentioned above – analysis is limited to small samples, unless fragments or test pieces are available for study. While no-one would argue that, for example, immersing a young paint sample in solvent is representative of a cleaning treatment, simplified experiments can be valuable in identifying principles of solvent action. The limitations of such studies must be recognised, however, and the results put in context with data obtained from the study of paintings.

Samples from paintings have an additional drawback that they are more poorly defined in terms of composition, and this may have been altered to some extent by previous conservation treatments, either from the removal of components by cleaning agents or the introduction of additional materials such as varnishes and consolidants, which will complicate interpretations further. For these reasons, treatment based studies of solvent effects are likely to be more empirical or limited in scope.

The current research is an attempt to integrate both approaches, of model studies and object-based experiments, and is concerned with the solvent extractable components of oil paint films, using these as an indicator of the risks associated with solvent cleaning. Specifically, of interest are the long term risks – embrittlement, optical effects – which have been associated with solvent leaching: more immediate risks, such as the increased potential for mechanical damage as a consequence of swelling or softening of paint layers, will not be addressed in this study. (Swelling phenomena are the subject of ongoing research elsewhere [61].)
The intention is to build on the existing body of data on solvent leaching, to provide a clearer idea of the factors influencing the leaching process, and hence the cleaning situations which are likely to present a greater degree of risk; as well as to provide more information on how the behaviour of relatively young, test paint films relates to that of much older films.

Experiments have been based primarily on the study of laboratory-prepared paint films, with a range of ages from 3 to 65 years, none of which had undergone accelerated ageing. Where possible, results have been compared with analyses of samples from paintings, with examples studied between 150 and 750 years old. The comparative data is aimed at addressing questions such as how much solvent extractable material is present in considerably aged paint films, as compared to the younger test films; and how much can be extracted as a result of simulated conservation treatments (cleaning and varnishing), as compared to immersion in solvent. At the same time the importance of model studies is recognised in its own right, for identifying trends in solvent effects relating to factors such as solvent type, and age and pigmentation of the paint film, and for providing insights into the ageing and deterioration reactions that occur in drying oil. This is especially true in light of the improved understanding of drying oil chemistry which has come from recent research.

In Chapter 3, experiments to characterise the solvent extractable material from a variety of oil paint films will be described, and the relationship of the soluble components to the drying reactions of the oil discussed. The quantitation of the soluble components, using both measurements of change in weight and GC analysis of fatty acids; and the relationship of the quantities of extractable material to various factors, including paint film composition and the solvent used for extraction, will be addressed in Chapter 4. The specificity of different solvents, with regard to the type of material extracted, will also be discussed in this chapter.

Chapter 5 describes an investigation of the effects of varnishes in extracting soluble components from a paint film, and the influence of the resin component of the varnish on its solvent properties and leaching action, and Chapter 6 presents data from experiments to quantify the material extracted by cleaning tests on paintings, dating from the seventeenth to nineteenth centuries.

The methods of sample derivatisation used for GC analysis of fatty acids, and the adaptations made to the methods for these studies, will be discussed in Chapter 7.
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References

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