Solvent extractable components of oil paint films
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Citation for published version (APA):
Sutherland, K. R. (2001). Solvent extractable components of oil paint films
Summary

Organic solvents are the most widely used materials for cleaning paintings, that is, the removal of discoloured and deteriorated varnish and overpaint. They are also used in other painting conservation treatments, such as varnishing, inpainting and consolidation. Treatments of paintings using solvent generally involve some degree of risk to the original paint layers. As well as the most direct risks associated with highly solvent sensitive paint formulations, studies of model oil paint films exposed to solvent have demonstrated that processes of swelling and leaching can occur to varying degrees, for a range of pigmented and unpigmented oil film types. Swelling, from the absorption of solvent into the paint layer, can potentially produce a softened paint film for which there is an enhanced risk of mechanical damage during cleaning. To some extent this phenomenon can be judged empirically in the process of cleaning, and can be minimised through careful manipulation of cleaning solvents. Leaching refers to the extraction of organic components from the polymeric oil matrix, and its potential effects are longer term and less immediately tangible to the conservator: in studies, the effects of leaching have been found to include increased brittleness, a consequence of the leachable components having plasticising properties in the paint film; and changes in optical characteristics, resulting from disruption of binding medium at the paint surface.

A detailed understanding of these solvent effects is important to help conservators to predict, and minimise, the risks inherent in solvent treatment. In this thesis, which is concerned specifically with the phenomenon of leaching, the extraction of soluble components from a variety of pigmented oil films has been studied, to give an improved understanding of the different factors affecting the leaching process, the chemical nature of the extractable components, and the magnitude of leaching effects likely to be associated with practical treatments such as varnishing and cleaning.

There has been a long history of controversy associated with the cleaning of paintings, and aspects of the cleaning debate are described in Chapter 1, which puts research into solvent effects in the broader context of physical and chemical properties of painting materials, and methods used for cleaning. Some of the
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Recurrent issues in the debate are examined in this chapter from a technical standpoint, and the extent to which results from cleaning studies have been incorporated into the discussions is also considered.

A concern which has frequently been raised is for the value of studies of model paint films, and the extent to which results from such studies can be extrapolated to represent solvent effects on paintings of significant age. In the present study, experiments have been carried out both on laboratory-prepared oil paint films and on samples from paintings, dating from as early as the thirteenth century, to get some idea of the nature of the extractable components and the magnitude of solvent effects on these much older paint samples, as compared to the relatively young test paint films. The complementary nature of the two types of study are discussed in Chapter 2, which first gives a survey of research which has been carried out to date into solvent effects on oil paint films, including a brief summary of research concerned with other paint media, and the use of gelled/aqueous cleaning systems. Chapter 2 concludes with an overview of research described in subsequent chapters.

In order to study leaching, it is helpful to have an understanding of the chemical identity of the extractable components, and the relationship of these soluble compounds to the ageing and deterioration processes in the oil. Chapter 3 presents data from the characterisation of solvent extractable fractions from a variety of oil paint films of different age and pigmentation, using gas chromatography (GC), Fourier transform infrared spectroscopy (FTIR), size exclusion chromatography (SEC), liquid chromatography mass spectrometry (LCMS) and direct temperature resolved mass spectrometry (DTMS). Numerous compounds were identified, including free fatty acids, mono-, di- and triglycerides, as well higher molecular weight, oligomeric components in some samples. These various compounds are produced by the complex combinations of reactions – cross-linking, oxidative scission, hydrolysis, etc. – occurring in the drying oil. The relative proportions of the different components in solvent extracts vary according to factors such as pigmentation and age of the film, and the time of exposure to solvent.

Quantitative measurements are described in Chapter 4, in which the amounts of material extractable from different paint films were determined from both changes in weight, and using GC analysis of fatty acids in paint samples and solvent extracts. The quantities extractable, and rates of extraction, were found to depend on factors such as the pigmentation and medium content of the paint films, with greater amounts of extractable material found, and extraction occurring more rapidly, for paint films with slower drying pigments and high medium content.
Evidence was found for a progressive decrease in the proportions of acetone extractable fatty acids in lead white paint samples with age, for samples up to 65 years old. However, significant quantities of fatty acids were found to be extractable from paint samples as much as 700 years old.

The specific action of solvents, with regard to the types of material extracted, is also described in Chapter 4, with the more polar solvents in the study found to extract a greater proportion of the more oxidised, polar paint film components, and compounds of higher molecular weight.

Experiments designed to investigate the potential leaching effects of more "realistic" exposures to solvent, as in varnishing and cleaning treatments, for comparison with the more theoretical immersion studies discussed in Chapters 3 and 4, are the subject of the following two chapters. Chapter 5 describes experiments to measure the quantities of fatty acids extracted from a paint film by a solvent based varnish applied to the film. A series of varnishes were applied to sections of a model paint film, and the fatty acids extracted from the paint layer into the varnish were quantified from analysis of samples of the dried varnish, and of samples of paint before and after treatment. The amounts extracted were found to be related not only on the solvent used to apply the varnish, but also to the resin component, with the varnishes formulated with more polar, oxygenated resins (represented in the study by the chemically reduced ketone resin, MS2A, and dammar) found to have a greater leaching effect than those made from a nonpolar, hydrocarbon resin (Regalrez 1094). The results 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 paint layers from varnishing.

A number of treatment-based experiments, carried out on paintings dating from the seventeenth to nineteenth centuries, are described in Chapter 6. The experiments were carried out with an aim to measuring quantities of fatty acids extracted from paint layers as a result of solvent cleaning treatments, represented by local cleaning tests on the paintings. Paint samples were taken from cleaning test areas before and after solvent cleaning, and the quantities of fatty acids extractable from the samples by immersion in solvent (typically the cleaning solvent) were determined. Differences in the quantities extractable from samples taken before and after cleaning were used to indicate the magnitude of leaching effects. In some cases a small, but measurable proportion of fatty acids was found to be removed from the paint layers by cleaning, but in others the effect was too small to be reliably determined. This was despite prolonged exposure to polar solvents in most of the tests. The results indicate that although a considerable amount of extractable material can remain in significantly aged paint films, only a
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very small proportion of this appears to be removed by exposure to solvent in the form of a single cleaning treatment.

Gas chromatography was used extensively in this study for qualitative and quantitative analysis of fatty acids in paint samples and solvent extracts. Chapter 7 gives details of the methods used for methylation of fatty acids for GC analysis – using the reagents diazomethane and TMTFTH ((m-trifluoromethylphenyl) trimethylammonium hydroxide) – and describes some of the relative advantages of the two reagents. The adaptations made to standard derivatisation procedures for quantitative measurements – of the proportions of fatty acids in extract samples present in the form of free acids and glyceride esters, and the quantities of solvent extractable fatty acids as a proportion of total fatty acids in a paint sample – are also described.