Introduction

It is of fundamental concern to conservators, curators and others who have responsibility for works of art, that conservation treatments applied to the works in their care should be safe, reliable and predictable. These responsibilities apply very compellingly to methods of cleaning used for easel paintings and have perhaps been the subject of more debate than any other conservation procedure [1]. The congress on *Cleaning, Retouching and Coatings* held in Brussels in 1990 is evidence of this widespread interest within the conservation world. There were, however, no reported studies of the effects of organic solvents on actual surfaces of paintings [2]. The use of organic solvents and solvent mixtures for the removal of old discoloured or otherwise degraded natural- and synthetic-resin varnishes from old master paintings has a long history, probably at least 300 years [3], and remains a standard method of cleaning in use by conservators around the world [4]. Before the seventeenth century, methods for removing degraded varnish from pictures involved a variety of abrasive and chemical treatments, often with alkaline agents, and these methods were undoubtedly damaging to the paint surface.

Although empirical observation suggested that no damage was being done by the use of organic solvents, no studies on the effects of the cleaning solvents—as now employed in the removal of varnish from old master paintings, conducted under the conditions used in conservation studios—have been published. Data gathered from solvent interactions with artificially aged test paint films have been interpreted to infer degradational changes in surface paint layers on pictures [5]. These inferences of damage, however, have been vigorously contested and remain of no proven application to pictures of significant age, that is, for oil paintings more than a hundred years old. In addition, the relevance of test paint samples which have undergone accelerated aging as a model in cleaning studies has been the subject of considerable debate [6].

GC-MS AND SEM STUDIES ON THE EFFECTS OF SOLVENT CLEANING ON OLD MASTER PAINTINGS FROM THE NATIONAL GALLERY, LONDON

Raymond White and Ashọk Roy

Studies in Conservation **43** (1998) 159–176

Summary—*This paper adopts a new approach to cleaning research, made possible by recent developments in sample derivatization. For the first time, an extensive analytical study has been made of the solvent cleaning of a range of paintings from the early fifteenth century to the end of the nineteenth century. Direct analytical comparisons are made between samples from mechanically and solvent-cleaned test areas of both tempera and oil paintings, using gas chromatography-mass spectrometry (GC-MS) and scanning electron microscopy (SEM).*

STUDIES ON THE EFFECTS OF SOLVENT CLEANING ON OLD MASTER PAINTINGS FROM THE NATIONAL GALLERY, LONDON

Raymond White and Ashok Roy

Studies in Conservation **43** (1998) 159–176

Redacted version of title and abstract

Summary—*This paper adopts a new approach to cleaning research, made possible by recent developments in sample derivatization. For the first time, an extensive analytical study has been made of the solvent cleaning of a range of paintings from the early fifteenth century to the end of the nineteenth century. Direct analytical comparisons are made between samples from mechanically and solvent-cleaned test areas of both tempera and oil paintings*

Overview of experimental work

Our work to investigate the effects of solvent cleaning on paintings has followed a dual path: one based on chemical analysis, the other involving a microscopical approach. The purpose has been to attempt to discover whether changes in the chemical composition of the surface paint layers of a painting on cleaning can be detected by sensitive methods of organic analysis, principally examination of minute samples by gas chromatography-mass spectrometry (GC-MS), and at the same time whether paint texture changes induced by solvent cleaning can be detected in the scanning electron microscope (SEM). In the first case, the principle was to examine areas of paintings cleaned of varnish by mechanical means and compare these to adjacent areas cleaned using solvents; in the second, paint samples from adjacent areas before and after cleaning were imaged at high resolution in the SEM. Organic analytical work of this precision has become possible only in recent years on samples of the very small sizes that can be taken from valuable paintings and is largely the result of improvements in instrumental sensitivity coupled with improved derivatization methods, developed for paint media in the Scientific Department of The National Gallery [7].

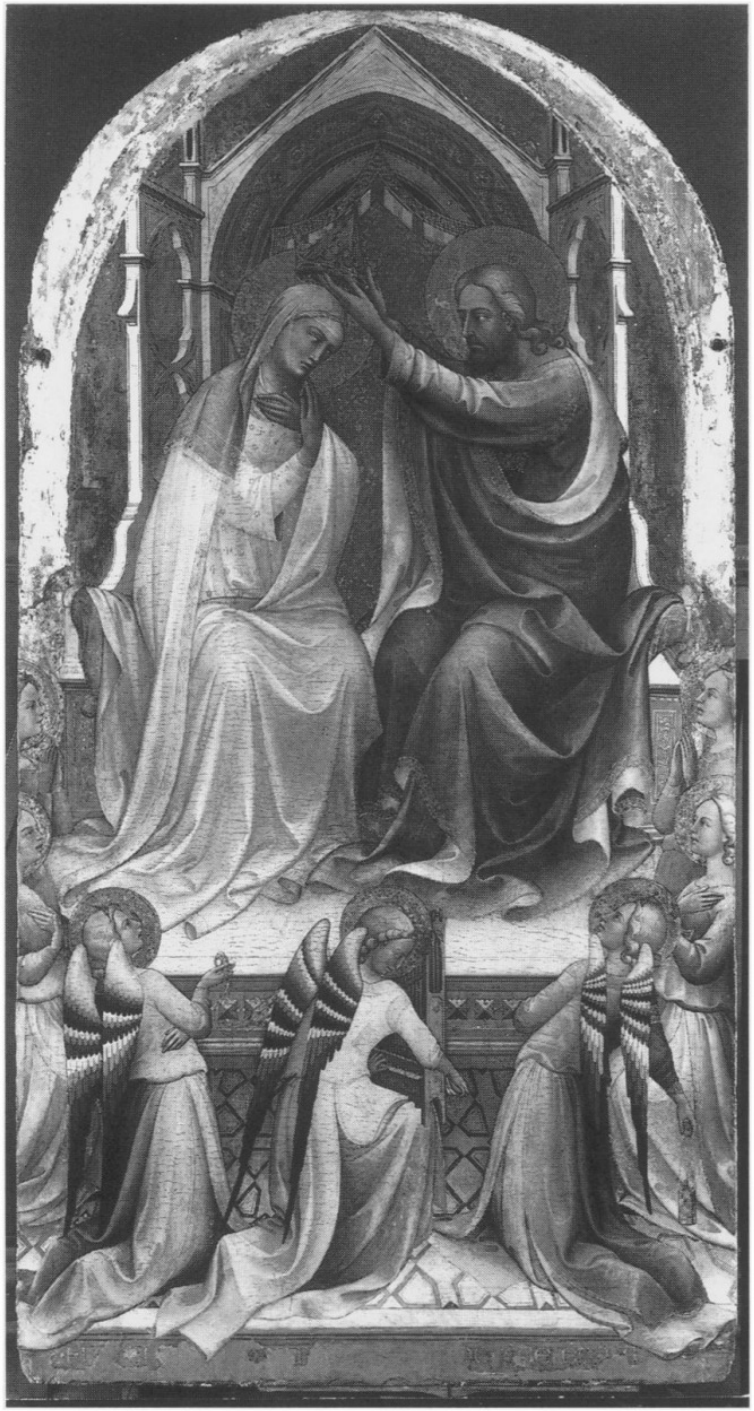

Figure 16 Lorenzo Monaco, 'The Coronation of the Virgin', No. 1897.

Results

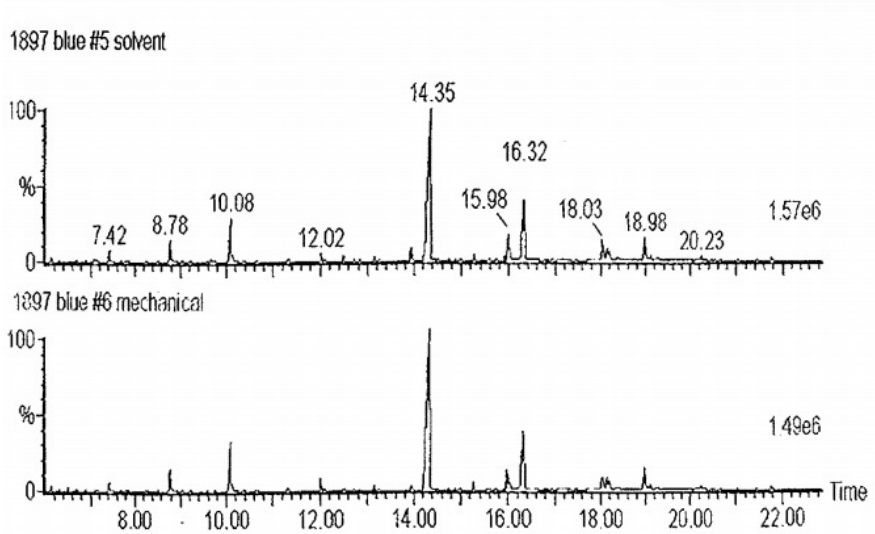

Figure 17 No. 1897: comparison TIC chromatograms of solvent-cleaned (upper trace) and mechanically cleaned (lower trace) dark blue paint of Christ's robe.

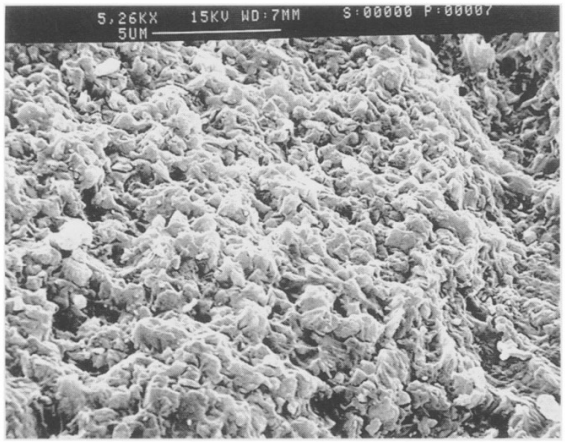

Figure 28 Lorenzo Monaco, 'The Coronation of the Virgin', No. 1897. SEM micrograph of pale greyish-mauve of Virgin's drapery. Interior of paint layer, c. 10μm depth from surface, to show microtexture. Before cleaning, 5260×.

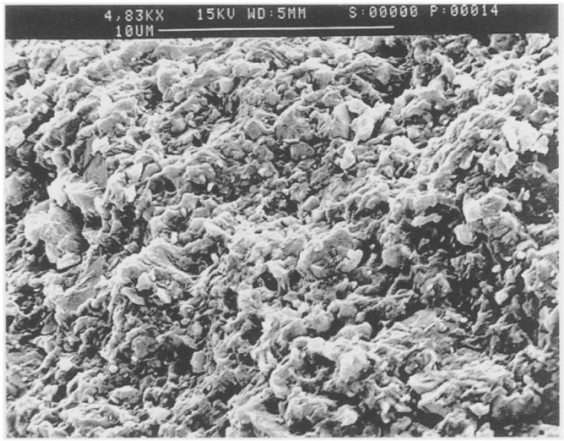

Figure 29 As Figure 28, adjacent area, after cleaning, 4830×.

Conclusion

The results of the GC-MS study on directly comparable paint samples from areas of pictures following solvent and mechanical removal of varnish are clear and unambiguous in that unlike young paint test films, which have undergone accelerated aging, there was no evidence for the leaching of potentially plasticizing low molecular weight components from the crosslinked paint binder matrix. This was even more reassuring in view of the considerably more direct and severe exposure to solvent action in the case of test areas which were either mechanically stripped of varnish prior to solvent action, or where, as in some cases, two sets of solvents or solvent mixtures were allowed to act on the paint, in quick succession. Such insignificant differences as were detected between solvent and mechanical cleaning were certainly of no greater magnitude than the natural fluctuations observed in different samples of the same paint area taken after mechanical cleaning. In no case was any bias evident which pointed to a selective removal of the lower molecular weight scission products down to nonanoic acid. Smaller fragments than these, such as lower acids and ketones, would have appreciable vapour pressure at room temperature and would of their own accord migrate from the film, and would be of little consequence in old, established paint films. Their plasticizing effects would be short-lived and of no importance in easel paintings which are more than a few decades old.

These studies cannot be designed to detect or identify the effects on old paintings of past cleanings, whether these involved solvents or treatments with other reagents, or in cases where quite different methods were used. The conclusions of the analyses described here are based on cleaning techniques as they are carried out by trained conservators, and the results are interpreted as offering support for the safety of solvent cleaning as it is practised at present. The results of paint texture examination in the SEM support these general conclusions and have a particular bearing on potential changes in the optics of paint films on cleaning, such as the light-scattering effect that the formation of voids at or near the surface would produce. In a wide range of picture types, no evidence from SEM imaging was found for physical damage to the internal structure of paint layers as a result of extraction of material when the surface was swabbed with organic solvents.

We conclude, therefore, that to the limits of sensitivity of the methods of examination employed here, in the hands of experienced conservators, solvent cleaning of old master paintings, which are painted in conventional egg tempera and drying oil media, is a controllable conservation treatment that is unlikely to cause damage as a result of the removal of original material from the paint film.