

Solvent Leaching Effects on Aged Oil Paints

Ken Sutherland

ABSTRACT. This paper presents a survey of significant developments in research on the leaching of oil paint films by organic solvents, from the first systematic investigations carried out in the 1950s to more recent “clinical” studies involving the sampling and analysis of paintings during treatment. Key studies are discussed in the context of an improved knowledge of oil paint chemistry that has developed in recent decades and advances in analytical techniques that have allowed a more informed and precise analysis of the solvent-extractable components of aged oil paints. Current research related to solvent cleaning effects, including studies of the formation of metal soaps and their migration in oil paints and the leaching effects of aqueous cleaning systems on acrylic paint media, is considered. The challenges of interpreting experimental data in relation to cleaning practice are outlined and illustrated with reference to discussions of research on solvent effects in the conservation literature.

There must have been many . . . who wishfully hoped the phenomenon [leaching] could be dismissed as an insignificant curiosity only of interest to the scientist, perhaps conveniently to be soon forgotten.

—Rees Jones (1973:43)

Organic solvents have long been the most widely used materials for the removal of discolored or deteriorated varnish and retouchings from paintings, a complex operation prosaically known as “cleaning.” The leaching of oil paint films by solvents, that is, the extraction of soluble, non-cross-linked components of the binding medium, was first described in detail by Nathan Stolow in a series of influential publications in the 1950s–1970s (Stolow, 1957a, 1957b, 1963, 1971). The findings of Stolow and other researchers were widely discussed by conservators and museum scientists and became a controversial component of the more general debate on cleaning (for a detailed review of solvent cleaning studies, see Phenix and Sutherland, 2001). The above remarks by Stephen Rees Jones were made in a review of the second edition of the book *On Picture Varnishes and Their Solvents*, in which Stolow summarized his research, and they convey the uncertainty with which the findings on leaching were initially received. Unlike the related phenomenon of swelling, which carries the acute risk of softening and disruption of paint, the risks associated with leaching are less immediately tangible to the conservator and have proved to be more contentious in discussions of cleaning. In the early experiments by Stolow and others, carried out on laboratory-prepared oil paint films, leaching was found to result in embrittlement of the films and optical changes (blanching or desaturation) of paint surfaces. Although highly significant, such risks are difficult to assess in practice. Changes

in mechanical properties resulting from cleaning are likely to be gradual and long term, and any blanching of the paint film caused by roughening of the surface on a microscopic scale will be masked by the overlying varnish, making it almost impossible to determine if a blanched condition revealed by cleaning is pre-existing or exacerbated by the new treatment.

The challenge of translating the experimental data into conservation practice can be illustrated by comments from conservators, in which very different interpretations are drawn regarding how best to minimize solvent effects such as leaching. In 1968, Ruhemann (1968:198) responded to Stolow's findings by suggesting "we must do our cleaning thoroughly instead of, by semi-cleaning, inciting renewed and unnecessary repetition." Emile-Mâle (1976:72), in contrast, interpreted the leaching phenomenon as supporting a more cautious approach of varnish reduction (*allègement*), remarking "this prudent method is used for reasons that are both aesthetic and technical . . . [so as to] avoid putting solvent in contact with the color layer since its binder would become impoverished" (Emile-Mâle's specific reference to leaching is clarified in a note [1976:122]: "It's a matter of the lixiviation or impoverishment of an old binder in contact with the solvent, without [any] effect on the polymerized component but entraining/extracting the decomposition products"; translations are the author's).

These conflicting viewpoints demonstrate a tendency, in the absence of a complete understanding of solvent effects in practice, to adopt the research results selectively to rationalize personal cleaning preferences, in this case, the approaches of "total" and "partial" cleaning, as characterized by Hedley (1985). Similar arguments to those of Emile-Mâle, that the advantages of a less thorough approach to cleaning include a reduction in the risk of leaching, have appeared more recently (Rothe, 2003:15; Modestini, 2005). The opinions are grounded in valid concepts: Ruhemann, for example, defended his preference for complete cleaning using solvents such as acetone by stressing the importance of the rate of solvent action with respect to diffusion and evaporation (Ruhemann, 1968:201). Factors such as evaporation were indeed downplayed in the early leaching studies, which generally involved immersion of paint samples in solvent for considerable periods. With respect to partial cleaning, a residual (swollen or partly dissolved) varnish must certainly provide some protection from mechanical action of a solvent swab on the paint surface, but the argument that leaching and swelling will also be minimized is tenuous. Stolow's experiments demonstrated that because of the rapid penetration of solvents, the response of paint films coated with a varnish layer was virtually the same as that of uncoated films (Stolow, 1971:58). Furthermore, subsequent studies have shown that a solution of varnish can itself have a measurable leaching effect on a paint film (Tsang and Erhardt, 1992:89–90; Sutherland, 2000).

Another concept that received some renewed attention in the early discussions of leaching was the possibility of replasticizing, or "nourishing," paint films by the application of some kind of nonvolatile, nondrying substance to replace the material

extracted by solvent (Stolow, 1963:88; Ruhemann, 1968:198; Sutherland, 2001:39). The idea was expressed more recently by Leonard (2003:227; in this case describing the treatment of a painting in egg tempera): "my own thoughts . . . were that use of a natural resin . . . was somehow appropriate because it would literally feed or renourish the surface with materials similar to those that had been leached out," although allowing that this was "an admittedly romantic notion that may not be founded in scientific fact." As Leonard suggests, we know too little about the penetration of varnish or other materials into the paint structure on a molecular level to speculate that such surface treatments might have physical and not just aesthetic benefits to the paint layers. As with the previous comments, the lack of a precise understanding of leaching effects or how they can best be minimized or remedied in practice perhaps invites such conjecture.

The more we learn about the material structure of paintings through technical study, the more we appreciate their true complexity.

—Zuccari (2003:252)

A major obstacle to the general acceptance of the results of cleaning studies has been the criticism that the relatively young, laboratory-prepared paint films used in many of the experiments are not sufficiently representative of paint films hundreds of years old in terms of their chemical and physical structure and hence their response to solvents. Roy's (2003:30) recent remark that "there are no good models of Old Master paintings that can be used for cleaning studies" echoes numerous earlier opinions, including Laurie's (1935:34) blunt verdict that "experiments made on recent oil films are useless." As will be discussed, the importance of well-designed experiments on model paint films cannot be dismissed so readily. However, the general concern has been validated to some extent by research in recent decades that has provided an improved knowledge of the complex chemistry and long-term aging behavior of oil paints.

Stolow's interpretations of his swelling and leaching data were based on a model of a dried oil paint film derived from then-current knowledge of film formation in drying oils. He described the dried film as a network of cross-linked triglycerides, incorporating a low molecular weight fraction, the leachable components, comprising glyceride monomers, partially polymerized species (e.g., dimers), and small molecules produced by oxidative scission. Hydrolysis of the glycerides, now known to be a major component of the aging process, was not considered, and pigments were discussed only generally, in terms of their role in the catalysis or retardation of the drying process, and not as an integral and chemically reactive part of the paint structure (Stolow, 1971:50–54). Such a model may have been reasonable for many of the younger paint films Stolow used in his experiments, and it provided a convincing explanation of the behavior he observed. However, the model does not accurately represent the significantly aged paint films that are typically encountered

in practice. Recent studies have shown that processes such as hydrolysis of the oil medium and the formation of ionic bonds between the resultant carboxylic acid groups and constituents of inorganic pigments play a substantial role in the formation of a mature paint film (van den Berg et al., 1999; Erhardt et al., 2000). The dynamic nature of paint films has been emphasized, with further alterations such as pigment dissolution, the migration of metal carboxylates, and their remineralization within the paint structure occurring in some cases (Boon et al., 2002; van Loon, 2008). The improved understanding of natural aging processes in oil paints provided by studies such as these encouraged a reassessment of experimental data on solvent effects and a more critical evaluation of their relevance to cleaning (Phenix, 2002). Risks associated with the use of more polar solvents and aqueous cleaning agents such as chelators, which may selectively disrupt ionic interactions in the paint film, could be greater than previously acknowledged (Phenix and Burnstock, 1992; Mansmann, 1998; Phenix, 2002; van den Berg, 2002:45–52). New concerns have been expressed, such as the possible role of organic solvents in promoting the migration of fatty acid carboxylates (metal soaps) within or between paint layers, processes that can have a significant impact on a painting's appearance (Noble and Boon, 2007:11). Given these various factors, the precise mechanisms of swelling and leaching and their interrelationship appear considerably less straightforward than Stolow proposed.

We look forward to the day when measurements can be made of the soluble material leached out in actual restoration.

—Ruhemann (1964:39)

A notable development in research on solvent cleaning was the use of case studies involving direct observations of paintings during treatment. This was made possible in part by improvements in instrumental methods for the analysis of organic paint materials, which allowed precise measurements to be made of the composition of the paint binder and solvent extractable components, rather than relying on parameters such as the weight and dimensions of paint samples to indicate solvent effects. At the same time, an object-based approach has certain limitations, notably the lack of a precise knowledge of the original paint formulations and the influence of past conservation treatments on the paint composition, which must be taken into account when interpreting the data. A systematic investigation was carried out at the National Gallery, London, in the 1990s (White and Roy, 1998), in which samples were taken from old master paintings in the course of solvent cleaning and were analyzed by gas chromatography mass spectrometry and scanning electron microscopy to investigate possible changes in the organic composition and physical structure of the paint layers. The comparative analyses did not provide evidence for alterations as a result of cleaning in the cases studied. A similar approach was taken by this author, but using quantitative gas chromatographic measurements of solvent-extractable fatty

acids in samples taken from paintings before and after cleaning (in the form of local varnish removal) to investigate possible leaching effects (Sutherland, 2001, 2006). These experiments, carried out on paintings dating from the seventeenth to nineteenth centuries, indicated a small but measurable extraction of fatty acids in some cases but no observable effect in others. This was despite prolonged cleaning using polar solvents in most of the tests.

The results of these studies suggest that for paint films of significant age (hundreds of years old) exposed to solvent in normal practical situations, leaching likely occurs at very low levels. It is important to note that although the leaching effect of an individual cleaning treatment may be minimal, a painting will undergo numerous campaigns of cleaning and varnishing in its lifetime, and the cumulative impact of these treatments must be borne in mind. Experiments have established that substantial quantities of organic material can be extracted from paint films hundreds of years old by immersion in solvent, well in excess of the amount removed by a single cleaning (Sutherland, 2006), refuting the opinion that any extractable material will be removed in the first exposures of a painting to solvent and that cleaning of previously treated paintings is unlikely to have a further effect (Ruhemann, 1968:305; Mancusi-Ungaro et al., 2003:113).

Although the low levels of leaching found in these experiments are reassuring when compared to the more extreme responses observed with the immersion of test paint films in solvent, the findings do not undermine the value of research using laboratory-prepared films. Despite their limitations, test films with precisely known composition and aging conditions, not to mention their availability in relatively large quantities, allow systematic investigations of factors such as the paint composition (pigment and oil type) and the relative effects of different types of solvent exposure. Such controlled experiments thus provide an essential theoretical basis for the applied studies. In general, the findings from studies of paintings, taken together with data from laboratory-prepared test films, support conventional wisdom in cleaning that repeated or prolonged exposure to solvents should be minimized as much as possible and underscore the principle of employing stable and reversible materials in conservation treatments.

We are dealing with complex objects and we should not expect to find easy solutions.

—Hedley (1989:136)

The significance of leaching in relation to cleaning remains a contentious question. In 1989 Hedley (1989:136) expressed optimism about the future of cleaning science, and although our knowledge of oil paint aging and solvent effects has advanced since Stolow's landmark research, the suggestion of Koller (2000:7) that "a balanced and complementary understanding of the problems of cleaning finally seems to have been reached" is perhaps too idealistic. Cleaning research continues to face both practical and conceptual problems: that is, in the execution of

the research and in its communication and translation into usable concepts.

The practical challenges inherent in studying cleaning effects can be further illustrated by another current area of research: aqueous cleaning of acrylic paintings. There is a growing body of information on the extraction of soluble material from acrylic paint films, as summarized in a recent review (Ormsby and Learner, 2009). The use of laboratory-prepared films is less controversial in this area of research than is the case for oil paintings since many acrylic paintings requiring cleaning are still relatively young and presumably closer in chemical and physical structure to the model paint films used for the tests. However, assessing the implications of alterations to the paint films involves very different considerations. The components identified in extracts from acrylic films are principally surfactants and other additives, whose primary role is the stabilization of the liquid dispersion and whose long-term influence on the properties of the dry paint is less well understood, as acknowledged by Smith (2005:824): “the potential benefits or detriments of removing these components are as yet unknown.”

With respect to oil paintings, the general response to leaching appears to have been one of cautious acceptance that, to some degree, this is an inevitable risk in cleaning, one that must be considered alongside other risks when making a decision to clean a painting. There has been progress in our understanding of the nature and magnitude of solvent effects on aged paint films, notably that, in the examples tested, superficial exposures to solvent such as in cleaning treatments appear to have a minimal leaching effect on paint films hundreds of years old. These findings are encouraging and help to place the earlier, theoretical studies in a more practical context. However, given the challenges of making accurate measurements on samples from paintings, it has not yet been possible to draw more specific conclusions regarding the relative risks involved in different cleaning treatments in practice or for different paint formulations. For such comparisons we are still reliant on data from model paint films in combination with the empirical experience of the conservator.

The continued application of sensitive analytical techniques to understanding the effects of solvent cleaning will doubtless overcome some of the technical difficulties discussed. Future research should place more focus on alterations at the very surface of the paint layer since many of the measurements to date have been of bulk film properties; again, this can be attributed to the daunting methodological challenges in measuring subtle changes at a microscopic level. An improved understanding of surface phenomena would clearly be valuable, as these are most critical with respect to the painting's appearance.

REFERENCES

- Boon, J. J., J. van der Weerd, K. Keune, P. Noble, and J. Wadum. 2002. “Mechanical and Chemical Changes in Old Master Paintings: Dissolution, Metal Soap Formation and Remineralization Processes in Lead Pigmented Ground/Intermediate Paint Layers of 17th Century Paintings.” In *ICOM Committee for Conservation, 13th Triennial Meeting, Rio de Janeiro, Preprints*, ed. R. Vontobel, pp. 401–406. London: James & James.
- Emile-Mâle, G. 1976. *Restauration des peintures de chevalet*. Fribourg, Switzerland: Office du Livre.
- Erhardt, D., C. S. Tumsa, and M. F. Mecklenburg. 2000. “Natural and Accelerated Thermal Aging of Oil Paint Films.” In *Tradition and Innovation: Advances in Conservation*, ed. A. Roy and P. Smith, pp.65–69. London: International Institute for Conservation.
- Hedley, G. 1985. On Humanism, Aesthetics and the Cleaning of Paintings. Two lectures delivered at the Canadian Conservation Institute, Ottawa. Reprinted in C. Villers, ed. 1993. *Measured Opinions: Collected Papers on the Conservation of Paintings*, pp. 152–166. London: United Kingdom Institute for Conservation.
- . 1989. Recent Developments in Cleaning. Introductory speech delivered at workshop in New Methods of Cleaning Paintings, Courtauld Institute of Art, London. Reprinted in C. Villers, ed. 1993. *Measured Opinions: Collected Papers on the Conservation of Paintings*, pp. 135–136. London: United Kingdom Institute for Conservation.
- Koller, M. 2000. Surface Cleaning and Conservation. *The Getty Conservation Institute Newsletter*, 15(3):5–9.
- Laurie, A. P. 1935. Restrainers and Solvents Used in Cleaning Old Varnish from Pictures. *Technical Studies in the Field of Fine Arts*, 4(1):34–35.
- Leonard, M. 2003. “The Restoration of a Predella Panel by Luca di Tommé.” In *Early Italian Paintings: Approaches to Conservation*, ed. P. S. Garland, pp. 225–232. New Haven, Conn.: Yale University Press.
- Mancusi-Ungaro, C., Z. Véliz, S. Schaefer, and A. Roy. 2003. “Panel Discussion.” In *Personal Viewpoints: Thoughts About Paintings Conservation*, ed. M. Leonard, pp. 110–115. Los Angeles: The Getty Conservation Institute.
- Mansmann, K. 1998. Oberflächenreinigung mit Ammoniumcitrat. *Zeitschrift für Kunsttechnologie und Konservierung*, 12(2):220–237.
- Modestini, M. 2005. John Brealey and the Cleaning of Paintings. *Metropolitan Museum Journal*, 40:27–36.
- Noble, P., and J. J. Boon. 2007. Metal Soap Degradation of Oil Paintings: Aggregates, Increased Transparency and Efflorescence. *AIC Paintings Specialty Group Postprints*, 19:1–15.
- Ormsby, B., and T. Learner. 2009. The Effects of Wet Surface Cleaning Treatments on Acrylic Emulsion Artists' Paints—A Review of Recent Scientific Research. *Reviews in Conservation*, 10:29–41.
- Phenix, A. 2002. The Swelling of Artists' Paints in Organic Solvents. Part 2, Comparative Swelling Powers of Selected Organic Solvents and Solvent Mixtures. *Journal of the American Institute for Conservation*, 41:61–90. <http://dx.doi.org/10.2307/3179897>.
- Phenix, A., and A. Burnstock. 1992. The Removal of Surface Dirt on Paintings with Chelating Agents. *The Conservator*, 16:28–38. <http://dx.doi.org/10.1080/01400096.1992.9635624>.
- Phenix, A., and K. Sutherland. 2001. The Cleaning of Paintings: Effects of Organic Solvents on Oil Paint Films. *Reviews in Conservation*, 2:47–60.
- Rees Jones, S. 1973. Book Review: *On Picture Varnishes and Their Solvents*, Revised and Enlarged ed. *Studies in Conservation*, 18:43–44. <http://dx.doi.org/10.2307/1505541>.
- Rothe, A. 2003. “Croce e Delizia.” In *Personal Viewpoints: Thoughts About Paintings Conservation*, ed. M. Leonard, pp. 13–25. Los Angeles: The Getty Conservation Institute.
- Roy, A. 2003. “Comments.” In *Personal Viewpoints: Thoughts About Paintings Conservation*, ed. M. Leonard, p. 30. Los Angeles: The Getty Conservation Institute.
- Ruhemann, H. 1964. Book Review: *Über die Erhaltung von Gemälden und Skulpturen*. *Studies in Conservation*, 9:38–41. <http://dx.doi.org/10.2307/1505119>.
- . 1968. *The Cleaning of Paintings: Problems and Potentialities*. New York: Frederick A. Praeger.
- Smith, G. D. 2005. “A ‘Single-Shot’ Separation and Identification Technique for Water Extractable Additives in Acrylic Emulsion Paints.” In *ICOM Committee for Conservation, 14th Triennial Meeting, The Hague, Preprints*, ed. I. Verger, pp. 824–832. London: James & James.
- Stolow, N. 1957a. The Action of Solvents on Drying Oil Films: Part I. *Journal of the Oil and Colour Chemists' Association*, 40(5):377–402.
- . 1957b. The Action of Solvents on Drying Oil Films: Part II. *Journal of the Oil and Colour Chemists' Association*, 40(6):488–499.
- . 1963. “Application of Science to Cleaning Methods: Solvent Action Studies on Pigmented and Unpigmented Linseed Oil Films.” In *Recent Advances*

- in *Conservation: Contributions to the IIC Rome Conference, 1961*, ed. G. Thomson, pp. 84–88. London: Butterworths.
- . 1971. “Solvent Effects.” In *On Picture Varnishes and Their Solvents*, rev. and enlarged ed., pp. 47–116. Cleveland, Ohio: Case Western Reserve University.
- Sutherland, K. 2000. The Extraction of Soluble Components from an Oil Paint Film by a Varnish Solution. *Studies in Conservation*, 45:54–62. <http://dx.doi.org/10.2307/1506683>.
- . 2001. Solvent Extractable Components of Oil Paint Films. Ph.D. thesis, University of Amsterdam, Amsterdam.
- . 2006. Measurements of Solvent Cleaning Effects on Oil Paintings. *Journal of the American Institute for Conservation*, 45:211–226.
- Tsang, J.-S. and D. Erhardt. 1992. Current Research on the Effects of Solvents and Gelled and Aqueous Cleaning Systems on Oil Paint Films. *Journal of the American Institute for Conservation*, 31:87–94. <http://dx.doi.org/10.2307/3179615>.
- van den Berg, J. D. J. 2002. Analytical Chemical Studies on Traditional Linseed Oil Paints. Ph.D. thesis, University of Amsterdam, Amsterdam.
- van den Berg, J. D. J., K. J. van den Berg, and J. J. Boon. 1999. “Chemical Changes in Curing and Ageing Oil Paints.” In *ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, Preprints*, ed. J. Bridgland, pp. 248–253. London: James & James.
- van Loon, A. 2008. Color Changes and Chemical Reactivity in Seventeenth-Century Oil Paintings. Ph.D. thesis, University of Amsterdam, Amsterdam.
- White, R., and A. Roy. 1998. GC-MS and SEM Studies on the Effects of Solvent Cleaning on Old Master Paintings from the National Gallery, London. *Studies in Conservation*, 43:159–176. <http://dx.doi.org/10.2307/1506743>.
- Zuccari, F. 2003. “The Conservation of Early Italian Paintings at the Art Institute of Chicago.” In *Early Italian Paintings: Approaches to Conservation*, ed. P. S. Garland, pp. 251–257. New Haven, Conn.: Yale University Press.