Smithsonian Institution
Scholarly Press

SMITHSONIAN CONTRIBUTIONS TO MUSEUM CONSERVATION • NUMBER 3

New Insights into the Cleaning of Paintings

Proceedings from the Cleaning 2010 International Conference Universidad Politécnica de Valencia and Museum Conservation Institute

Edited by
Marion F. Mecklenburg, A. Elena Charola, and Robert J. Koestler

SERIES PUBLICATIONS OF THE SMITHSONIAN INSTITUTION

Emphasis upon publication as a means of "diffusing knowledge" was expressed by the first Secretary of the Smithsonian. In his formal plan for the Institution, Joseph Henry outlined a program that included the following statement: "It is proposed to publish a series of reports, giving an account of the new discoveries in science, and of the changes made from year to year in all branches of knowledge." This theme of basic research has been adhered to through the years by thousands of titles issued in series publications under the Smithsonian imprint, commencing with Smithsonian Contributions to Knowledge in 1848 and continuing with the following active series:

Smithsonian Contributions to Anthropology
Smithsonian Contributions to Botany
Smithsonian Contributions to History and Technology
Smithsonian Contributions to the Marine Sciences
Smithsonian Contributions to Museum Conservation
Smithsonian Contributions to Paleobiology
Smithsonian Contributions to Zoology

In these series, the Institution publishes small papers and full-scale monographs that report on the research and collections of its various museums and bureaus. The Smithsonian Contributions Series are distributed via mailing lists to libraries, universities, and similar institutions throughout the world.

Manuscripts submitted for series publication are received by the Smithsonian Institution Scholarly Press from authors with direct affiliation with the various Smithsonian museums or bureaus and are subject to peer review and review for compliance with manuscript preparation guidelines. General requirements for manuscript preparation are on the inside back cover of printed volumes. For detailed submissions requirements and to review the "Manuscript Preparation and Style Guide for Authors," visit the Submissions page at www.scholarlypress.si.edu.

SMITHSONIAN CONTRIBUTIONS TO MUSEUM CONSERVATION • NUMBER 3

New Insights into the Cleaning of Paintings

Proceedings from the Cleaning 2010 International Conference Universidad Politécnica de Valencia and Museum Conservation Institute

Edited by
Marion F. Mecklenburg, A. Elena Charola, and Robert J. Koestler

Smithsonian Institution
Scholarly Press
WASHINGTON D.C.
2013

ABSTRACT

Mecklenburg, Marion F., A. Elena Charola, and Robert J. Koestler, editors. New Insights into the Cleaning of Paintings: Proceedings from the Cleaning 2010 International Conference, Universidad Politécnica de Valencia and Museum Conservation Institute. *Smithsonian Contributions to Museum Conservation*, number 3, x + 243 pages, 142 figures, 22 tables, 2013.— The present volume brings together the papers and posters presented at the "Cleaning 2010 International—New Insights into the Cleaning of Paintings" conference that was held at the Universidad Politécnica de Valencia in Spain, in collaboration with the Smithsonian's Museum Conservation Institute. This was the first major international conference on this topic in two decades. The 20 papers and 19 extended abstracts presented at the conference are included in this publication, grouped into four main categories: Ethics, Aesthetics, Training, and Documentation; Traditional Media: Egg Tempera and Oil; Modern Paints; and Cleaning Systems. Within each category, the papers and extended abstracts are grouped by the specific topic they address to make it easier for the reader to find all related material in one section. A summary of panel discussions held at the end of the conference has also been included. All papers and abstracts included in this publication have been peer reviewed. The aim of the conference was to provide a knowledge exchange forum and to produce a publication that assembles the latest developments in the various studies addressing the problems that affect paintings. These range from normal soiling to removal of aged varnishes, from the effect of solvents on paints to the subsequent changes in their mechanical behavior. The cleaning of unvarnished paintings is one of the most critical issues that was discussed. Finally, different cleaning techniques, such as gels, soaps, enzymes, ionic liquids, and foams, as well as various dry methods and lasers, are discussed in various papers and extended abstracts. Although the conference was organized in Spain, the United States contributed 21% of the contents, followed by Spain and Italy, both with 16%; the United Kingdom and Germany, each with 9%; and Canada, the Netherlands, and Portugal, all with 5%. The rest are individual contributions from Australia, Norway, Switzerland, Poland, and Greece.

Cover images, from left to right: Figure 1 from García and Marín; Figure 1 from Cremonesi; and detail of Figure 1 from Osmond and Carter.

Published by SMITHSONIAN INSTITUTION SCHOLARLY PRESS
P.O. Box 37012, MRC 957
Washington, D.C. 20013-7012
www.scholarlypress.si.edu

Compilation copyright © 2013 Smithsonian Institution

The preface and acknowledgments are in the public domain. The rights to all other text and images in this publication, including cover and interior designs, are owned either by the Smithsonian Institution, by contributing authors, or by third parties. Fair use of materials is permitted for personal, educational, or noncommercial purposes. Users must cite author and source of content, must not alter or modify copyrighted content, and must comply with all other terms or restrictions that may be applicable. Users are responsible for securing permission from a rights holder for any other use.

Library of Congress Cataloging-in-Publication Data

Cleaning International Conference (2010 : Valencia, Spain)

New insights into the cleaning of paintings : proceedings from the Cleaning 2010 International Conference, Universidad Politecnica de Valencia and Museum Conservation Institute / edited by Marion F. Mecklenburg, A. Elena Charola, and Robert J. Koestler.

pages cm. — (Smithsonian contributions to museum conservation, ISSN 1949-2359 ; number 3)

Includes bibliographical references and index.

1. Painting—Cleaning—Congresses. 2. Painting—Conservation and restoration—Congresses. I. Mecklenburg, Marion F., editor of compilation. II. Charola, A. Elena, editor of compilation. III. Koestler, Robert J. (Robert John), 1950– editor of compilation. IV. Title.

ND1650.C43 2012

751.6'2--dc23

2012041342

ISSN: 1949-2359 (print); 1949-2367 (online)

♾ The paper used in this publication meets the minimum requirements of the American National Standard for Permanence of Paper for Printed Library Materials Z39.48–1992.

Contents

PREFACE vii

ACKNOWLEDGMENTS ix

ETHICS, AESTHETICS, TRAINING, AND DOCUMENTATION

The Removal of Patina 1
Stephen Gritt

Considerations of the Cleaning of Paintings 7
Konrad Laudenbacher

The Art and Science of Cleaning Paintings 11
Stephen Hackney

Surface Cleaning of Paintings and Polychrome Objects in Italy: The Last 15 Years 17
Erminio Signorini

Extended Abstract—A Preliminary Investigation into the Surface Characteristics of Paint and the Implications for Restoration 23
Laurent Sozzani

Extended Abstract—Noncontact and Noninvasive Monitoring of Overpaint Removal with Optical Coherence Tomography 27
Magdalena Iwanicka, Dagmara Kończalska, Piotr Targowski, and Bogumiła J. Rouba

Extended Abstract—A New Documentation System: Stratographic Units Recording Sheets Applied to the Cleaning of a Fifteenth-Century Painting 31
José Manuel Barros García and Eva Pérez Marín

Extended Abstract—Computer Applications and Cleaning: Teas Fractional Solubility Parameter System in Conservation 35
Amparo Saera Vila and José Manuel Barros García

TRADITIONAL MEDIA: EGG TEMPERA AND OIL

The Chemistry of Egg Binding Medium and Its Interactions with Organic Solvents and Water 39
Antonella Casoli, Michela Berzioli, and Paolo Cremonesi

Solvent Leaching Effects on Aged Oil Paints 45
Ken Sutherland

Oil Paints: The Chemistry of Drying Oils and the Potential for Solvent Disruption 51
Charles S. Tumosa and Marion F. Mecklenburg

The Influence of Pigments and Ion Migration on the Durability of Drying Oil and Alkyd Paints 59
Marion F. Mecklenburg, Charles S. Tumosa, and Edward P. Vicenzi

Effects of Organic Solvents on Artists' Oil Paint Films: Swelling 69
Alan Phenix

An Evaluation of Color Change in Nineteenth-Century Grounds on Canvas upon Varnishing and Varnish Removal 77
Meredith Watson and Aviva Burnstock

Extended Abstract—Oxalate-Rich Surface Layers on Paintings: Implications for Interpretation and Cleaning 85
Ken Sutherland, Beth Price, Andrew Lins, and Irma Passeri

MODERN PAINTS

Characterization and Stability Issues of Artists' Alkyd Paints 89
Rebecca Ploeger and Oscar Chiantore

The Nonideal Action of Binary Solvent Mixtures to Oil and Alkyd Paint: Influence of Selective Solvation and Cavitation Energy 97
Stefan Zumbühl, Ester S. B. Ferreira, Nadim C. Scherrer, and Volker Schaible

Sensitivity of Oil Paint Surfaces to Aqueous and Other Solvents 107
Hannah Tempest, Aviva Burnstock, Polly Saltmarsh, and Klaas Jan van den Berg

Extended Abstract—The Effect of Conductivity on Water Solubility: Cleaning a Modern Chinese Oil Painting 115
Gillian Osmond and Anne Carter

Extended Abstract—Noninvasive Assessments of Cleaning Tests on an Unvarnished Oil Painting on Canvas by Edvard Munch 119
Tine Frøysaker, Mirjam Liu, and Costanza Miliani

Multitechnique Approach to Evaluate Cleaning Treatments for Acrylic and Polyvinyl Acetate Paints 125
María Teresa Doménech-Carbó, Miguel F. Silva, Elvira Aura-Castro, Antonio Doménech-Carbó, Laura Fuster-López, Jose V. Gimeno-Adelantado, Stephan U. Kröner, María Luisa Martínez-Bazán, Xavier Más-Barberá, Marion F. Mecklenburg, Laura Osete-Cortina, and Dolores J. Yusá-Marco

Extended Abstract—A Preliminary Study into the Effects of Cleaning Polyvinyl Acetate Paints 135
Ana Pereira, Maria João Melo, Peter Eaton, Stephan Schäfer, and Tom Learner

The Modular Cleaning Program in Practice: Application to Acrylic Paintings 139
Chris Stavroudis and Tiarna Doherty

Cleaning of Acrylic Emulsion Paints: Preliminary Extractive Studies with Two Commercial Paint Systems 147
Richard Wolbers, Amanda Norbutus, and Anthony Lagalante

Surfactants and Acrylic Dispersion Paints: Evaluating Changes Induced by Wet Surface Cleaning Treatments 159
Bronwyn Ormsby, Elli Kampasakali, and Tom Learner

Extended Abstract—Effects of Solvents on the Physical Properties of Polymeric Films 165
Mareike Opeña and Elisabeth Jägers

Extended Abstract—The Removal of Commercial Varnishes from Acrylic Paints 169
Marie-Catherine Cyr, Emily Min, and Alison Murray

Extended Abstract—Cleaning Issues for Nine Francesc Artigau Pop Art Paintings 175
Anna Nualart-Torroja, Marta Oriola-Folch, and Marina Mascarella-Vilageliu

CLEANING SYSTEMS

Rigid Gels and Enzyme Cleaning 179
Paolo Cremonesi

Effects of Commercial Soaps on Unvarnished Painted Surfaces: A Pilot Study for Their Assessment 185
Andrés Sánchez-Ledesma, Carmen Muro-García, and María Dolores Gayo-García

Extended Abstract—Tissue Gel Composite Cleaning 197
Gwendoline Fife, Jos Van Och, Kate Seymour, and Rene Hoppenbrouwers

Extended Abstract—Partially Hydrolyzed Polyvinyl Acetate and Borax Gels for Cleaning Painted Surfaces 201
Lora V. Angelova, Barbara H. Berrie, and Richard G. Weiss

Extended Abstract—Use of Agar Cyclododecane for Cleaning Tests on a Frail Painting 205
Alberto Finozzi, Alessandra Sella, and Chiara Stefani

Dry Cleaning Approaches for Unvarnished Paint Surfaces 209
Maude Daudin-Schotte, Madeleine Bisschoff, Ineke Joosten, Henk van Keulen, and Klaas Jan van den Berg

Extended Abstract—The Schlürfer: A Vacuum Technique for the Cleaning of Paintings 221
Ina Hausmann and Petra Demuth

Extended Abstract—Surface Cleaning with Aqueous Foams 225
Anne Heckenbücker and Petra Demuth

Extended Abstract—Residues on Unvarnished Surfaces after Absorene Sponge Dry Cleaning 229
Shawn Digney-Peer and Julie Arslanoglu

Extended Abstract—The Use of Ionic Liquids for Varnish Removal: Effectiveness and Risk Evaluation 233
Maria Filipa Pacheco, Ana I. Pereira, A. Jorge Parola, and Luís C. Branco

Extended Abstract—Laser Cleaning Applied to Contemporary Paintings: Optimization of Working Parameters 237
Grazia De Cesare, K. Melessanaki, P. Pouli, J. Domingues, F. Rosi, C. Miliani, and C. Fotakis

ENDING NOTE: SUMMARY OF PANEL DISCUSSIONS 239
Jacqueline Ridge

INDEX 241

Preface

Paintings are among the oldest manifestations of human culture. The conservation of this heritage has long concerned mankind, and the most critical and frequent operation required is that of cleaning. Cleaning involves not only the removal of accumulated dirt from the painted surface but also the removal of aged varnish that had been applied to protect the paint layer(s).

In May 2010 a conference called "Cleaning 2010 International" was held at the Universidad Politécnica de Valencia in Spain, in collaboration with the Smithsonian's Museum Conservation Institute. This was the first major international conference on this topic in over two decades. The 20 papers and 19 extended abstracts presented at the conference are included in this publication, grouped into four main categories: Ethics, Aesthetics, Training, and Documentation; Traditional Media: Egg Tempera and Oil; Modern Paints; and Cleaning Systems. Within each category, the papers and extended abstracts are grouped by the specific topic they address to make it easier for the reader to find all related material in one section. All papers and abstracts included in this publication have been peer reviewed.

The opening section, Ethics, Aesthetics, Training, and Documentation, serves as an introduction to the subsequent technical sections; it is a guiding principles section and is complemented by those papers that address the training of conservators as well as documentation issues during the cleaning intervention. The first paper, by Stephen Gritt of the National Gallery in Canada, addresses the removal of patina, presenting a historical look at the varying approaches to this issue. The second paper, by Konrad Laudenbacher, former Head Conservator of the Doerner Institut in charge of the Neue Pinakotheke in Munich, provides the insight of a long life devoted to paintings conservation. He discusses the threats that accompany any conservation intervention as well as the even bigger risks to which paintings are subjected when they are moved for exhibition. Popular international exhibitions that circulate among major museums make these masterpieces accessible to a large number of people worldwide, but there is a definite cost in terms of the risk to the art, and it is feared that these costs are not correctly balanced. The third paper corresponds to the keynote lecture presented by Stephen Hackney of the Tate Museum addressing the art and science of cleaning paintings. This paper covers a wide area, ranging from art historical to ethical and technical issues, and highlights the importance of interdisciplinary collaboration.

The second and third sections are separated by the nature of the paint used for the paintings, that is, into traditional painting media and into modern developed paints, although they may share many of the same problems, such as the interaction with solvents. The last section deals with different cleaning techniques, such as gels, soaps, enzymes,

ionic liquids, and foams, as well as various dry methods and lasers. Some improvements that aid in the application of these methods are also presented.

The notion of conservation in general can be considered an ideal neoromantic notion. The desire to preserve an object that is known to be perishable for as long as possible is utopian but probably universally comprehensible. It is especially understandable in an era when changes occur so rapidly that parents and children are practically living in two different technological worlds. And for those of us working in museums, it is an obligation.

A. Elena Charola
Robert J. Koestler
Museum Conservation Institute, Smithsonian Institution

Acknowledgments

This publication would not have been possible without the enthusiasm and support provided by Paula T. DePriest. Many others contributed indirectly through their support during the preparation of these proceedings. Among them we thank Laura Fuster-López from the Universidad Politécnica de Valencia, Spain, and Carol Grissom and Ann N´Gadi from the Museum Conservation Institute for their help during the long process of getting the various papers into the required format. Last but not least, we thank Ginger Strader, director of the Smithsonian Institution Scholarly Press, for her perseverance and patience during the review process of this issue.

The Removal of Patina

Stephen Gritt

ABSTRACT. From the beginning of historic discussions of any appropriate look for old paintings, patina was a critical term and was principally used to add legitimacy to darkened or discolored surface coatings. As the use for paintings, their marketplaces, and treatment procedures developed, tensions evolved around this issue, reaching pressure points during various cleaning controversies. Attitudes toward appropriate look have always been indexed to physical understanding of paintings, and the capabilities of cleaning procedures and treatment technologies historically have been a principal driver within the debate. Today, we have an expanded array of capability and a generous conception of our objects and the materials that comprise them. The notion of patina is no longer a critical term within the professional discourse, partly as a result of this. Aesthetic mediation during cleaning is no longer a central matter of stated attitude or dogma and appears to be less commonplace than in the past, although we are now technologically more capable.

INTRODUCTION

The title here does not refer to the removal of material, but to the fact that the term "patina" and its traditional accompanying connotations are no longer critical within discourse about the cleaning of paintings. I am not saying it is not still an active notion, and I am not saying this is a bad thing, but it is interesting that it has become noncritical. Historically, it has been central to discourse within the profession of restoration, mostly because as a conception, any notion of it was intimately connected to understanding the possibilities of cleaning, the dangers of cleaning, and the aging of valued objects. The term patina has become increasingly irrelevant or fragmented as a coherent notion, as cleaning technologies and our understanding of paint have developed.

PRIOR TO THE NINETEENTH CENTURY

One early use of the term patina in relation to paintings was by Baldinucci in 1681 in his *Vocabulario toscano dell´arte del Disegno* (Kurz, 1962:56): "A term applied to paintings, otherwise called a skin, it is a general darkening that time makes appear over the painting, that sometimes improves it." This is not the first reference to the term in texts and commentaries of the seventeenth century, but it is the one most frequently cited, largely because it appears to offer no judgment (the book is essentially a glossary), and during the 1960s it was used by protagonists of different viewpoints in debates over the

***Stephen Gritt**, National Gallery of Canada, 380 Sussex Drive, P.O. Box 427, Station A, Ottawa, Ontario K1N 9N4, Canada. Correspondence: sgritt@gallery.ca.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

cleaning of paintings. This definition, along with other instances of discussion of the effects of time, indicates consideration of change in paintings, but limited to overall darkening at the surface. It is logical that this kind of commentary became part of the dialogue on painting at that time since the seventeenth century was a period when great collections were formed, an international art market reached maturity, and canonical and collectible paintings began showing some age.

The predominant view during this period, it would appear, was that as paintings aged, they became more mellow and "soft" and tended to "ripen" and improve with time as they become more "unified," or harmonious. The principal rationalization of this type of change was that it was normal and natural and that time would "give more beauties, than he takes away" (Dryden, 1694). A refinement on this view was that these effects were expected by painters, who in some instances painted with "excessive freshness" in anticipation of them.

The majority of the described effects can be attributed, for the most part, to the darkening of varnish and the accumulation of dirt. The use of the term patina implies that the effect is superficial, as does the use of the word skin, of course, but what is interesting is that the effects, the mellowing, are conceived of as intrinsic to, or inseparable from, the paintings themselves. Practically, this was largely true: it would have been more or less impossible to safely (by our terms at least) remove a discolored surface coating from a painting in the seventeenth century.

During the eighteenth century, commentary continued in the same vein. From our perspective, there are two interesting comments to make.

First, although the effects of time clearly continued to be generally praised and valued, we begin to see in both private and official commentaries and exhortations that patina should be preserved. There is only one reason that its preservation would require advocacy, and this must have some relation with the cleaning of paintings, and consequent damage, becoming more commonplace. For instance, Algarotti wrote a letter in 1744 that was a general criticism of "modern taste" that "on the pretext of revivifying old paintings, the canvases of Tintorretto and Titian are frequently removed of their unity, that so precious patina that subtley unites the colours, and makes them more soft and more delicate, and that alone can give to pictures the harmony and venerability of age" (see Algarotti, 1823:145–150).

This criticism was directly related to the rise of institutional restorations and the emergence of the notion of cultural heritage, to say nothing of the practical realities of cleaning paintings at the time. An early instance of this occurred in Venice, where a combination of strong state and governance, rich heritage, a vital art market, and problematic environments occasioned early official supervision of restorations. Decrees of 3 January and 28 May 1730 concerned the institution of a systematic program of restoration, which put the men carrying out the work under the direct authority of the Collegio Veneto di Pitture and accountable to the Treasures of the Sal. In 1762, we find the Magistrates of the Sal making this official recommendation (Muraro, 1962):

> By excessive insistence on separating the patina beyond which is required, the masterful strokes would be worn away, and lost, as can so easily happen; these admirable canvases therefore sadly losing their intactness and universal aspect, their harmony and relationships that constitute their greatest virtue.

It was stated explicitly that patina should be preserved for sensible practical reasons to avoid changing or damaging a painting. In this, the notion formally accumulated one of its more complex connotations: that it is a marker of "authenticity," although this was likely to have always been implicit to some degree.

The second point to make is that although there is much general commentary on the aging of paintings, it is almost entirely focused on overall darkening. We know there was knowledge of changes occurring within paint films and that different pigments change differently, but this complex issue did not critically become part of the debate. An exceptional passage from William Hogarth's (1753) *Analysis of Beauty* is worth requoting here, with a note that it forms part of a general attack on the mindless veneration of historic painting, with no commentary on how to deal with the problem, intellectually or practically.

> When colours change at all, it must be somewhat in the manner following, for as they are made some of metal, others of earth, some of stone, and others of more perishable materials, time cannot operate on them otherwise than as daily experience we find it doth, which is, that one changes darker, another lighter, one quite to a different colour, whilst another, as ultramarine, will keep its natural brightness . . . Therefore how is it possible that such different materials, ever variously changing . . . should naturally coincide with the artist's intention.

THE NINETEENTH CENTURY

There is, of course, no one dominant attitude to cleaning throughout the nineteenth century. What seems to characterize the writings and commentaries as the century progresses is a gradual increase in professionalism, a greater scope of thought, increasing scientific research, and, to some extent, a certain amount of codification of practice.

The most significant factors in this are the fact that this century sees the rise of the public and the national museum and the shifting of commentary into more public arenas. Various cleaning controversies are one symptom of this change. Although we may rightly characterize nineteenth-century taste as being for generally mellow surfaces, we must acknowledge a significant change in attitudes. A representative example is this passage by Horsin Deon (1851:54), an officially appointed restorer to the French national museums.

> Respect for antiquity does not consist in the conservation of grime that covers the works of an old master

> and conceals its beauties. It is in the conservation of the works, in the cares that preserve them from the accidents that can shorten their life. Every master belongs to civilisation: It has duties that are imposed on their owners and guardians. That the amator dreamer likes the "rust" and blemishes of a varnish we are aware; for the varnish becomes a veil behind which the imagination of the amator can see what it wants to . . . But in a museum such as ours, the first in the world, the paintings must be seen sincerely and cleanly.

In some sense, we see here a shift in the notion of "authenticity" that will gain capital as the century progresses and reach a problematic conclusion in the middle of the twentieth century. In terms of the mid-nineteenth-century cleaning controversies that occurred in London and Paris, centered around treatment of paintings at the National Gallery and the Louvre, we see the issues laid out quite clearly, providing a blueprint for subsequent cleaning controversies. Under a banner of fear of removal of original material, restorations were criticized, but criticized for the loss of features such as "subordination," "glow," and "harmony," the result being "crudeness" and "primitive tones" in the cleaned paintings. In both cases the museums under fire made concessions and seem to have modified practices, but with official documentation and personal statements asserting that no original material had been removed or damaged and that the issues at stake were those of taste. Frederick Villot, deposed but ultimately promoted superintendent of restorations at the Louvre, asked the following question three years after the Paris debacle (Villot, 1860:54; my translation): "Do I not have reason to say that when one vaunts the patina of a painting, it is to go into false ecstasies, it is to recognize that it has lost all finesse of nuance, all variety of tone?"

Of the more important advances in conservation and restoration made during the nineteenth century were the researches into the techniques and materials of painting, both scientific and historical. These led to increased knowledge of the mechanisms and nature of degradation and change in paintings and, subsequently, an interest in preventive conservation. We also see a more generous and subtle appreciation of the changes paintings undergo during aging where previously the condition of a painting was more likely to be assessed in terms of the optical effect of a degraded varnish and the degree of loss.

This deeper understanding brings with it, however, more subtle conflict: how do we cope with the fact that the most prized residues of the best human activity may be very different from when they were made? Strategies varied between denial that the changes are significant and advocacy that paintings should be removed of all nonoriginal material to a reformed view of the value of patina since in cleaning paintings we would be "disillusioned if we returned them to their original freshness" (Dinet, 1924) because it was assumed that harmony was a quality of all old masters and most modern painting and because the tonal and chromatic suppression of an overall discolored surface coating was thought preferable to revealed discord. This view in its most extreme expression would claim that a painting unified by patina would be closer to how the artist intended than a changed painting totally cleaned.

In this we were likely seeing the beginning of polarization between camps of "total cleaning" and "partial/selective cleaning," as delineated by Hedley, which reached fruition in the second half of the twentieth century (Hedley and Viliers, 1993). We also see, as we move into the twentieth century, the beginning of a claim frequently and persistently made to this day that practicing contemporary painters have special expertise to add. Although this had long been implicit (the affectionate friendship between Delacroix and Villot was certainly cooled by the latter's supervision of restorations at the Louvre, for instance), it gained added force for many as restorers emerged as a distinct professional class, separate from painters who ended up restoring paintings.

From the point of view of notions of patina on paintings and critical discourse on the cleaning of paintings, the second half of the twentieth century is certainly the period of most intense and interesting debate. In terms of actual years, we might point to the period between 1947, the year of the National Gallery of London's "Exhibition of Cleaned Paintings," and the Brussels IIC conference of 1990, "Cleaning, Retouching and Coatings" (Mills and Smith, 1990). For many of us this dialogue is old news, and it is too fractured, various, and vital to review comprehensively here. Younger conservators and restorers may not be exposed during their training to this debate as different information assumes its place within curricula, and I can only encourage a detached anthropological review of our history as having an obvious, broad benefit. To attempt to summarize the terms of the debate would be foolish, but I do not mind that. In essence, all aspects of prior debate were brought together in an arena that forced historic and scientific research and personal and institutional viewpoints into close contact. On the one hand, we saw the formal emergence of a camp of total cleaning who thought that the painting stripped of all nonoriginal material was objectively closer to the intentional and authentic object than one obscured by dirt. On the other hand, there were several camps who argued coherently for a more generous conception of the historic object that was much changed from its intentional state and required mediation and judgment at all stages of any interaction, especially during cleaning. This is a much simplified view of the situation but captures the essence. At the heart of criticisms of the camp of total cleaning was the fear of removal of original material. At the heart of criticisms of mediating cleaning was the accusation of subjectivity and untruth. The issue of aesthetic danger lurked within and behind all this but rarely was compellingly brought to bear.

What has marked the last 20 years? One side of an optimal answer is easy: unparalleled research into the mechanisms and effects of degradation and the effects of our treatment procedures. This has been a major factor in moving beyond too much controversial debate, within the restoration profession at least, because it has clarified many of the issues and made dogmatic

standpoints difficult to maintain. In terms of identifiable trends, practice across institutions and in general has become closer in methodology and aims. The trend is for paintings to be cleaner today than previously but for the history of the object to be given more integrated, rational consideration. One contributing factor here is that knowledge about the nature of paint has also provided mechanisms for us to relativize change in paintings; we can, for instance, almost "enjoy" some forms of degradation, the discoloration associated with smalt, for instance, or the formation of lead soaps, aspects of old paintings that were rarely commented on before the 1990s, which we have learned to see. In essence, we have developed an information- or knowledge-based aesthetic for paintings that is a relatively new feature, and we should be aware of this. One very positive aspect of this is the emergence of the discipline of technical art history that is no longer marginal.

While I was thinking about these general issues in the context of the Cleaning 2010 International Conference, a small panel from Botticelli's workshop from around 1590 was being cleaned at the National Gallery of Canada. The painting depicts two small boys embracing, likely the infant Christ and St. John the Baptist. Purchased in 1927, the painting had received no treatment while at the National Gallery of Canada and had spent much of its Canadian life in storage. It came to the gallery with a recent dealer restoration on top of it, probably late nineteenth-century work, and presented two upper layers of varnish with extensive retouching, or overpaint, on top of an overall "gray layer." Some very old retouchings were present, but prior to treatment it was difficult to see at what layer these occurred. The first stages of the cleaning involved the separate removal of the two varnish layers with free-solvent mixtures; this method was chosen because it ultimately involved less solvent exposure than removal of the varnish in one operation. Examination of the gray layer quickly revealed it to have no early association with the paint, and exploratory testing indicated some sensitivity to very polar solvents, with an acetone-based solvent gel allowing full, controlled removal. The components and action of the gel were then isolated for further testing, and the gray layer was found to be slowly and safely removable simply with gelled water with an elevated pH. Numerous rectangular damaged areas to this layer and underlying paint, mostly areas of profound blanching, testified to an early twentieth-century desire and inability to safely remove it, likely using potent reagents. The earlier restorer had ultimately resorted to mechanical removal of the layer on certain highlights to reanimate the modeling, with consequent damage to paint and gesso. After the easy removal of the gray layer by simple aqueous poultice and a little patience, older retouchings and very polar residues of old varnish were removed with solvent gel and free solvent in conjunction with mechanical work. The removal of the tinted gray layer clearly revealed the presence of a dark stain at the surface of the paint in the shape of a stemmed flower, held in the hand of St. John. An intriguing scenario that suggests itself is that the shape is the ghost of an original or early rose that was repented and carefully removed while the paint was still wet. The use of a copper green in an oil-based medium would explain the staining of the surface and the suppression of fluorescence under UV, and the rose with its thorns has some iconographical relevance. Whatever the scenario, the stain likely was one of the reasons for the deliberate application of the gray layer since it largely concealed the confusing shape.

In many senses the cleaning methodology outlined here is representative of modern practice, and elements of this scenario will be familiar. From my perspective, an interesting aspect of this treatment is that although there was dialogue on retention of the gray layer between three conservators and curatorial staff, who had a great deal of knowledge of the true condition of the paint film beneath, all found the decision to remove the layer easy to make, despite the anticipated revelation of damage, the rose stain, and a faded pink paint. All felt total cleaning would bring the greatest benefit to the painting. I note that the decision to remove the layer was made after ascertaining that it could be done safely, and this is a critical issue. The new patina is, of course, our interest in interpreting or making sense of the stain and its link with the painting's history and even in the childish scratches in the surface, given paintings such as this were recommended for hanging in the rooms of children as an early introduction to religious imagery and education. The mediation of these factors during the restoration will constitute the painting's patina.

The restoration profession is perhaps in a new position: many of the classical dangers of cleaning can be obviated, and we know more about the risks and how to manage them. We can go way beyond the capabilities of our forebears with an enhanced range of options in cleaning that should produce more refinement, and perhaps it does. The technologies of cleaning have always been a major driver in how paintings end up looking, as is well known. It cannot be denied, however, that as a general tendency, as our ability to safely clean paintings increases, aesthetic mediation during cleaning appears to diminish. Technical capacity can make cleaning an entirely technical procedure. This may be a good thing, relatively speaking, but aesthetic mediation is certainly one aspect of the role of the restorer. To deny this would be illogical, given that what we do in cleaning and restoring paintings changes their appearance radically. Even if we can do it in a way that does not change them physically and our additions are safely reversible, this does not mean that what we do becomes less important.

We still have no good way to discuss aesthetic dangers, and that could be the next step in the evolution of restoration, although this has been historically very difficult. Discussion of this trips into subjectivity, and it requires great personal discipline to avoid this pitfall. One of the reasons we have not had significant contentious dialogue within this field recently is perhaps that we do not engage in aesthetically oriented discussion as much as we perhaps should. Possibly, with physical danger within treatment much reduced and with more generally shared practices and intentions, it may be time to reengage with the issue.

REFERENCES

Algarotti, F. 1823. Letter to Jacopo Bartolommeo Beccari, 16 May 1744. In *Opere scelte,* pp. 145–150. Milan: Dalla Società Tipografica de'Classici Italiani.

Deon, H. 1851. *De la restauration des tableaux*. [On the Restoration of Paintings.] Chapter 2. Paris: Hector Bossange.

Dinet, E, 1924. *Les fléaux de la peinture*: *Moyens de les combattre*. [The Scourge of Paintings: Means to Beat Them.] Paris: H. Laurens

Dryden, J. 1694. "To Sir Godfrey Kneller." In *Annual Miscellany.* London: R.E. for Jacob Tonson.

Hedley, G., and C. Viliers. 1993. *Measured Opinions: Collected Paper on the Conservation of Paintings*. London: United Kingdom Institute for Conservation.

Hogarth, William. 1753. *The Analysis of Beauty*. London: J. Reeves.

Kurz, O. 1962. Varnishes, Tinted Varnishes, and Patina. *The Burlington Magazine*, 104:56–59.

Mills, J. S., and P. Smith, eds. 1990. *Cleaning, Retouching and Coatings: Preprints of the IIC Brussels Congress*. ed. J. S. Mills and P. Smith. London: International Institute for Conservation.

Muraro, M. 1962. Notes on Traditional Methods of Cleaning Pictures in Venice and Florence. *The Burlington Magazine*, 104:475–477.

Villot, F. 1860. "Restauration des Tableaux du Louvre." In *Annuaire des Artistes et des Amateurs*, ed. P. Lacroix, pp. 265–274. Paris: Vve. Jules Renouard.

Considerations of the Cleaning of Paintings

Konrad Laudenbacher

ABSTRACT. The aim of this paper is to reshed some light on the broad subject of cleaning from the viewpoint of a museum conservator. One of the main reasons for cleaning or removing the varnish of a painting is a planned exhibition. This is surely not the most convincing reason for an intervention and can lead to more frequent restorations than necessary or desirable, often the fate of famous works of art. These actions are arguably the most controversial and dangerous restoration interventions that a painting will face. Such interventions are difficult because, on the one hand, the painting should not be touched if at all possible but, on the other hand, it is often unavoidable that work must be conducted directly on the painting. This means that the intervention, the effect of solvents, and any contact should stop exactly where the original paint layers begin. This cannot be guaranteed, either by traditional means or with modern materials and methods. The cleaning of a painting is more than a great physical risk for the work of art; under certain conditions it can also cause significant changes in its aesthetic appearance and perception. The success of an intervention, in particular, that of cleaning a work of art, thus depends on the cooperation between practitioners, art historians, and scientists, a partnership that is not always free of conflict. Relationships, historical facts, and questions of meaning must be collected and taken into account. This paper is intended to examine and enlighten the full range of issues encountered by professionals involved in the restoration of paintings, with particular emphasis on conservation ethics and the genesis of conservation treatment decisions.

PRELIMINARY CONSIDERATIONS

The objective of this paper is to reshed some light on the broad subject of cleaning from the viewpoint of a museum conservator. With the rapid developments in new cleaning techniques and analytical techniques in the last decade, it is important and necessary for the conservation community to constantly remind itself of the debate surrounding cleaning. In modern times, this debate began with the National Gallery of London "cleaning controversy" of 1947. Then, as now, it would be good for someone who spends much time looking at a few square centimeters of a painting through a microscope to go to the window and look out into the distance. Although the dedication to detail is understandable, one should not forget to look at the whole picture.

The success of an intervention, in particular, that of cleaning a work of art, depends on the cooperation between practitioners, art historians, and scientists, a partnership that is not always free of conflict. Relationships, historical facts, and questions of meaning must be collected and taken into account.

A painting can be unbelievably deterministic, fascinating, and powerful, analogous to and perhaps even more so than literature or music. On the other hand, the physical

***Konrad Laudenbacher**, Würth Museum, Künzelsau, Baden Württemberg, Germany. Correspondence: k.laudenbacher@gmx.de.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

substance and condition of a painting can make it extremely fragile, unstable, and sensitive.

The (surface) cleaning and the removal of varnishes are arguably the most controversial and invasive restoration interventions that a painting will undergo. Such interventions are difficult because, on the one hand, the painting should not be touched if at all possible, although, on the other hand, it is often unavoidable that work must be conducted directly on the painting. This means that the intervention, the effect of solvents, and any contact should stop exactly where the original paint layers begin. This cannot be guaranteed, either by traditional means or with modern materials and methods. The cleaning of a painting is more than a great physical risk for the work of art; it can also cause significant changes in its aesthetic appearance and perception under certain conditions.

HISTORICAL FRAMEWORK

A reading of the history and development of the means and methods for cleaning paintings in the past is still quite disturbing to those trained in modern conservation techniques and ethics. Suggestions for the use of various kinds of solvents already existed in the early nineteenth century. Their effect on picture surfaces was described by the early twentieth century (Doerner, 1921). In this publication, Doerner (1921:328–329) published warnings about the damage that could be caused by solvents and cleaning (my translation):

> There are countless cleaning materials, most of which are the secret of a particular conservator. One cannot believe all the possible types of materials which are applied to paintings! The strongest caustics, acids, and solvents are used without a second thought. Solutions with unknown composition, so-called secret solutions, are recommended to the public, as something anybody without any knowledge can use to clean pictures. Such "cleaning" methods are often too successful, right down to the ground layers. In those cases, the "conservator" covers up his sins by retouching. It is not uncommon that such locations appear cleaner to the unknowing public than the older version. Even to this day there are conservators who, in all seriousness, claim that they have cleaning materials which remove new paint but stop at the real, original layers. The only thing missing is that a bell should ring when the original paint layer is reached.

At the time, no one spoke of the removal of varnishes or cleaning, but of scrubbing, washing, and refreshing pictures. Caustics, acids, soaps, solvents, and ethereal oils were used. Every ingredient from the kitchen was put on the table: egg yolks, bread, vegetable juices, onions, garlic, and much more. Even now, instructions for restoration can be found in household manuals and guides for laymen. Rubbing a painting with half of a potato is often suggested.

By the mid-nineteenth century, questions and concerns about new painting techniques and approaches to cleaning paintings began to appear. These questions led to more contact with scientists in order to find a new fundamental starting point for interventions. This approach was sometimes successful; at other times it ended in failure. An example of the latter is the serious consequences of the regeneration process using alcohol and copaiba balsam vapor developed by Max von Pettenkofer, a Munich medical doctor, pharmacist, hygienist, and chemist (Schmitt, 1990). His procedure promised to be the solution for all problems related to the treatment of coatings and finishes and was long the fashion throughout Europe. He was named as the first scientist to head a commission dealing with restoration questions in 1862. He was cofounder of the German Society for the Promotion of Rational Methods in Painting (Deutsche Gesellschaft zur Förderung rationeller Malverfahren).

The use of balsams themselves for cleaning paintings, in particular copaiba balsam, was fashionable until the end of the nineteenth century. The effect of this balsam was devastating and catastrophic, especially on oil paintings (Urban, 1939; Schmitt, 1990). Copaiba balsam is a resin now known for its softening properties that remain active over a long period of time. An original paint layer treated with copaiba balsam is thus much more sensitive and subject to future damage than prior to the intervention. It is to be noted that commercial solutions such as Winsor and Newton Artists' Picture Cleaner still contain copaiba balsam.

The problems posed by cleaning paintings were the subject of extremely detailed, deep, and controversial discussions between conservators, scientists, and curators from 1947 to 1963 as a result of the exhibition Cleaned Pictures held at the National Gallery in London in 1947, the well-known cleaning controversy. For this exhibition, pictures underwent total and complete varnish removal, down to the paint layer. The paintings were, of course, analyzed exhaustively with the instruments and methods available at the time in order to assess their condition and identify later additions, such as overpainting and retouching. The objective of this controversial method was to recover the original appearance of the paintings to "bring the intention of the artists to light."

The discussions were at times polemic, the negative criticism prevailing in both professional circles and the public in general (Keck, 1984). The aesthetic changes and the new appearance were deplored by many. Directors of foreign museums argued that the radical and complete removal of varnish created the danger of damaging authentic materials by inducing irreparable damage and that the original condition of the picture could not be reached by the intervention. The National Gallery claimed, on the other hand, that it had taken great care in analysis, cleaning, and documentation and that there was no damage to the paint layers.

FURTHER CONSIDERATIONS

The arguments presented by the National Gallery are very similar to those expressed today. One of the main goals of

cleaning is still often defined as coming as close as possible to the original condition. Haag (1987:177–178) stated, "Restoration means bringing a work of art as close to its original appearance as the remaining material allows."

However, it cannot be emphasized sufficiently how complex such cleaning processes are and that individual and completely different aesthetic conceptions are not a responsible basis for making decisions concerning necessary restoration interventions. In fact, many dangers remain to this day.

Much progress has been made in the development of techniques for the analysis of binders and pigments since the time of the London controversy. Whereas scientists at the time could only identify protein-containing groups such as glues, egg white, etc., a far more detailed analysis is now possible. Scientists have looked more closely at solvents and cleaners and found that they can induce damage that is not readily visible. Information about the interactions and behavior of these materials has helped provide a better understanding of the effect of the application of solvents and has led to the development of alternative methods, such as special gels, soaps, tensides, and enzymes.

The reason for cleaning a painting or removing varnish is often a planned exhibition. This is surely not the most compelling reason for an intervention and can lead to more frequent restoration than necessary or desirable, often the fate of famous works of art. The wear of irreplaceable works of art will always be connected to large exhibitions that can be financed only if they travel to multiple venues. The damage that is unavoidably done to these irreplaceable works of art, even if the damage seems minimal at first, causes a huge loss in their life expectancy (Carlyle et al., 1990; Mansmann, 1998). This kind of attention casts a shadow on the conservator, scientist, art historian, patron, and the art business in general. How often has a work of art become the victim of publicity seekers?

It would be ideal if the conservator, when approaching a painting to be cleaned, were not influenced by the current restoration "fashion," the unavoidable "good taste," as these are products of the whims of time. However, these fashions still exist because conservators do not always recognize that they subconsciously apply contemporary taste to everything, including works of art, and that they are always dependent on current technical and intellectual resources and possibilities. As an example, the extension of the original use of ammonium citrate of varnished paintings to the surface cleaning of unvarnished classical modern paintings proved to be a damaging treatment procedure (Phenix and Burnstock, 1992; Mansmann, 1998). The same can be said for the development of artificial varnishes, which supposedly do not yellow or age. Ironically, many of them are not removable (Nicolaus, 1998; Koller and Baumer, 2001).

Unvarnished paintings are another point of contention. Varnishes and the cleaning of paintings are part of the lives of most classical works of art. On the other hand, many contemporary artists did not varnish their paintings. Many unvarnished pictures were trapped by the tastes of the time and were generously varnished, losing a certain important transparency. Victims include many classic modern and contemporary artists.

Then there is also a hierarchy of paintings. For example, pictures by Albrecht Dürer, Titian, or Diego Velazquez generally are damaged by accident or by overzealous treatments. Such works of art are almost always well treated and conserved as valuable treasures or, actually, are too well treated and often too conserved. Other paintings suffered more under the influence of the tastes of time or were forgotten, as is the case of works of Matthias Grünewald (circa 1480–1528), a contemporary of Albrecht Dürer and now recognized as the painter of the Isenheim Altarpiece. The question then remains as to how paintings of less significance are affected by treatments over time.

ACHIEVING THE OBJECTIVE

A short paper cannot possibly cover the entire discussion of the development of aesthetic, ethical, and scientific concepts of restoration. It is to be hoped that current restoration methods will provide a certain catalytic effect and direction that will help guide treatment decisions. Of course, the analysis of the binders, coatings, etc., that were used in past centuries has become more precise, and this makes restoration work far better informed. Also, more is known about the materials in use today. However, this should not be taken as a license to use these materials without thought. One should be careful not to rely entirely on science, which can convince us with unjustified certainty that currently available restoration materials and techniques are always much better than earlier methods. In particular, it is to be noted that the long-term effects of chemicals and solutions used today are still not known.

In order to achieve an optimal and objective result in restoration, art historians, scientists, and conservators must take an equal part in formulating the goals and methods for cleaning paintings, using technical, historical, and aesthetic aspects. It is important to realize that the combination of art historical and scientific research is optimally effective for a work of art when the participants respect each other's discipline to the same degree.

The critical preliminary steps before treatment are historical research and condition reporting. Treatises on paintings and their correct interpretation are an important source of information for preparing an intervention. The appearance that painted surfaces present is the result of many factors, including the techniques used by the artists and the aging and restoration history. The surfaces can be clear, tinted, matte, or glossy, and natural or artificial resins and oils may have been used. The subjects of glazes, glazing techniques, pigmented oil, and resin coatings and the materials used played an important role. These are discussed in many treatises on painting and are an important source of information for making judgments about cleaning (Schick, 1906). The excessive use of poppy seed oil and asphalt and also the individual painting technique of the artist are often the basis for the poor condition of many paintings. These situations have

occurred many times since the nineteenth century. Examples include works by Hans von Marée, Arnold Böcklin, and Joshua Reynolds. Hans von Marée painted an almost uncountable number (up to 70) of oil and tempera layers, one on top of the other. Böcklin had phases with wax techniques, did experiments with antique encaustics, painted with tempera, and used varnish. He was unbelievably innovative, to the detriment of conservators.

More importantly, a carefully prepared condition report must be the basis for every decision made during the subsequent restoration. It must contain all information about the work of art, including a precise listing of all visible phenomena without interpretation or judgment. Knowledge about topographic features, the various paintings traditions, and individual painting techniques and experiments is necessary. However, sources of information are often scarce. This is also one of the reasons why the Munich Pinakothek museums prefer in many cases to perform a careful reduction in the varnish rather than a total removal.

Cleaning interventions still run the risk of damaging the original paint layer and are the cause of the greatest changes in aesthetic appearance of paintings. Obviously, cleaning is always based on subjective criteria. However, the goal should still be to proceed on a historical basis and from technical as well as aesthetic viewpoints. The motto should be "first observe, then act." In order to fulfill the task of preserving the original, practical and technical skills, broad knowledge, and ethical principles serve equally as fundamental criteria for all restoration decisions. Only these criteria and their use can be the leading principle for a relatively objective work, free of the fashion of the time.

Art historians, scientists, and conservators share one thing in common: the painting under discussion. A discussion that focuses on an analysis of what a work of art is saying, what the artist intended, and what the artist's working and living conditions were as related to the society at the time should fascinate and enrich all participants.

BRIEF CONCLUSIONS

Less is more. On the basis of the experience at the Munich Pinakothek museums this is applicable to all areas of restoration and conservation. Conservators often have to deal with interventions that their predecessors performed in previous decades to the best of their knowledge and with the best methods at the time. These interventions have, in some cases, compromised the integrity of the paintings. Even if the gentler methods of the twenty-first century are used, conservators should be aware that they most likely will not be able to assess whether their work has been sufficiently gentle. However, there are no hard and fast rules. The best one can do is to be aware of the whole intervention, ask meaningful questions, and pay attention to associations and correlations. Although this should prove reassuring, it may also be disquieting.

Acknowledgments

I thank, first of all, my friend W. "Bill" Wei of the Netherlands Institute for Cultural Heritage, Amsterdam, for the translation, editing, and revising of this text. I also gratefully acknowledge Hans Otto Wiebus for revising the manuscript, as well as my colleagues and the photographers of the Doerner Institute for their support. Last but not least, thanks are owed to Laura Fuster-López, Teresa Domenech, and Ignasi Girones-Sarró of the Polytechnic University of Valencia for the invitation to the excellent Cleaning 2010 International Conference.

REFERENCES

Carlyle, L., J. Townsend, and S. Hackney. 1990. "An Investigation into Its Application for Surface Cleaning." In *Dirt and Pictures Separated,* ed. V. Todd, pp. 44–48. London: United Kingdom Institute for Conservation.

Doerner, M. 1921. Malmaterial und seine Verwendung im Bilde. [The Materials of an Artist and Their Use in Painting.] Reprint of 1938 6th ed. Stuttgart, Germany: Thomas Hoppe, 1993.

Haag, J. 1987. Entrestaurierung—Rückgewinnung von Authentizität oder Neuinszenierung. [Derestoration—Backwinning of Authenticity or New Scenario.] *Zeitschrift für Kunsttechnologie und Konservierung,* 1(1):177–178.

Keck, S. 1984. Some Picture Cleaning Controversies Past and Present. *Journal of the American Institute for Conservation*, 23(2):73–87. http://dx.doi.org/10.2307/3179471.

Koller, J., and U. Baumer. 2001. Niedermolekulare Kunstharze als Gemäldefirnisse [Low molecular weight artificial resins as painting varnishes]. *Restauro*, 107(1):26–38.

Mansmann, K. 1998. Oberflaechenreinigung mit Ammonium-citraten [Surface Cleaning with ammonium citrate]. *Zeitschrift für Kunsttechnologie und Konservierung,* 12(2):220–238.

Nicolaus, K. 1998. *Handbuch der Gemälderestaurierung.* [Handbook of Painting Restoration.] Cologne, Germany: Könemann Verlagsgesellschaft.

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.

Schick, R. 1906. "Tagebuch-Aufzeichnungen aus den Jahren 1866, 1868, 1869 über Arnold Böcklin." [Diary Notes from Years 1866, 1868, 1869 on Arnold Böcklin.] In *Böcklins Technik,* ed. E. Berger. Sammlung maltechnischer Schriften 1. Munich: Georg D. W. Callwey.

Schmitt, S. 1990. "Das pettenkofersche Regenerationsverfahren. Eine Studie zur Geschichte einer Methode und Ihren Auswirkungen." [The Pettenkofer Regeneration Procedure. A Historical Study of the Method and Its Effects.] *Zeitschrift für Kunsttechnologie und Konservierung,* 4(1):30–66.

Urban, H. 1939. Article cited as being in "Kameradschaft der Künstler München," *Bildende Kunst,* Heft 4. http://kremer-pigmente.de/62100-70150.htm (accessed 11 June 2012).

The Art and Science of Cleaning Paintings

Stephen Hackney

ABSTRACT. The topic of cleaning covers a large technical area of conservation that has been subject to periods of considerable controversy, which has constrained progress. The complexity of the technical debate on cleaning has limited useful discussion outside the conservation profession. To understand the subject in its entirety, many interpretive skills are required for a multidisciplinary approach. Scientific research, as demonstrated by the acrylics cleaning project, can provide conservators with better knowledge of materials, new ideas, and tools. A history of artist varnishing and conservation cleaning practice is limited by the paucity of literature and material evidence. Trends must be inferred from more recent practice. Developments in solvent, aqueous, and mechanical methods for varnish removal and for cleaning unvarnished surfaces are briefly discussed. Examination and analysis of paintings and materials are keys to understanding artists' methods more precisely and to interpreting their intentions better.

INTRODUCTION

The cleaning of a painting means the removal of any unwanted material that has been deposited on its surface since it was created, including any coatings applied initially to protect the surface that have subsequently deteriorated. This may be a varnish, even one applied by the artist, if its aging has changed the appearance of the object. It may also be any accumulation on its surface either from atmospheric deposition or by accretions of material from specific activities, perhaps of historic interest. Decisions on what or how much to remove must be taken in the context of a position on how the painting should look. The conservator's unique role is to contribute knowledge of what is technically feasible for the expectations of the results of cleaning. However, this is rarely how the problem is posed in everyday life.

In the past there have been several periods of intense interest and controversy, particularly on the subject of varnish removal, for example, the arguments surrounding Titian's *Bacchus and Ariadne* in the National Gallery in London in the 1960s and also the cleaning of wall paintings or ceilings, such as Michelangelo's Sistine Chapel. In all these cases the underlying argument is not technical but based on opinions on what the paintings should look like, and consequently, it is open to the views of a wide range of participants with significantly differing expertise and perspectives.

The technical debate has been almost entirely restricted to the conservation profession (Rees Jones, 1962). The experience of broadening discussion has not been rewarding since the complexity of the issues is sufficient to deter casual interest or even the

***Stephen Hackney**, Conservation Department, Tate Britain, Millbank, London SW1P 4RG, UK. Correspondence: stephen.hackney@tate.org.uk.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

valid concern of art history or museum professionals (Gombrich, 1962). Books aimed at a popular market have not obviously brought enlightenment (Walden, 1985). This problem extends to other professionals, such as art historians, museum directors, or artists, none of whom are likely to have the background knowledge to add significantly to the technical debate.

As a consequence, roles have developed that not only stifle debate but also allow the subject to be ignored. At one extreme the conservator is encouraged to make all the decisions, perhaps within a framework of institutional practice or previous work, and at the other the relationship between curator and conservator is one of art owner and contractor, where the conservator is expected to deliver a predetermined result. Clearly, neither of these extremes can be relied on to produce the best outcome.

Even within conservation, individual practitioners are not well equipped to understand the background science, and research scientists cannot expect to understand all the practical issues. In effect, the problem is truly multidisciplinary, and each individual can only deal with a part of it. Inevitably, in such a complex, unforgiving, and sometimes subjective area we tend to remain in our circle of comfort. Not many varnish removal specialists would feel that they have a complete overview of their field, and this extends to the subject of dirt removal from polychrome sculpture or modern paintings. So the Cleaning 2010 International Conference was a great opportunity to not only bring together the best expertise but also for each participant to learn more about unfamiliar aspects of cleaning (Phenix and Sutherland, 2001).

By single-mindedly concentrating on the undoubted technical challenge the conservation profession has not brought its technical knowledge to the wider ethical and aesthetic debate as effectively as it might have done (Hedley, 1993). Visual change to a painting after cleaning depends on many uncontrollable factors. The removal of an overall toning layer affects some pigments more than others, and the relationships between colors may change surprisingly. The nature of removed retouching and any replacements can have a greater visual effect on the treated painting than varnish removal. Understanding the nature and degradation of paintings unconnected with cleaning is essential since cleaning frequently uncovers problems not considered in the original decision to clean. Paintings change in many subtle and unquestioned ways, developing craquelure, becoming more transparent, and revealing pentimenti and tonal discrepancies. Pigments fade and mediums yellow or darken, and an increase in contrast between whites and darks revealed by cleaning can change the reading of perspective.

HISTORIC PRACTICAL FRAMEWORK

Cleaning starts with the decision to protect the surface. If an artist ignores the issue of dirt accumulation and the work is left unprotected, as is the case for many contemporary paintings, for example, color field paintings or acrylics, then dirt will be absorbed by the surface of the paint. Its removal may become a challenge or even impossible to carry out safely. At best, it will be difficult to predict the response of an unfamiliar paint to the method of cleaning, and if the work of art is an unforgiving unmodulated paint film, it may not allow the conservator any room for experiment or error. Several groups are making progress in the study of the problem of cleaning synthetic paints. The acrylic cleaning project is a good example of the conservation profession predicting and preempting a problem while there is still time to address it and options exist for a variety of solutions, including better prevention (Ormsby and Learner, 2009). It demonstrates the application of scientific method to a new and major conservation problem that requires radical innovation.

Historically, artists have protected oil painting surfaces with varnish, a system that allows the varnish to be brushed clean or even washed relatively frequently to remove accumulated surface dirt without exposing the paint to risk. Unfortunately, mastic or other traditional soft-resin varnishes do not last indefinitely. After a few decades the varnish becomes yellow and brittle, losing transparency, and the cleaning process is transformed into the more challenging problem of removing the degraded varnish directly from the picture surface. Even when new, a varnish changes the appearance of a painting. It increases the transparency of any partly coated pigments or low refractive index medium, and it imparts a new surface, which is frequently glossy. Mostly, artists have accepted such immediate changes in appearance for the future benefits of protection from dirt and from the risks of dirt removal. Inevitably, because of its sacrificial purpose, little early varnish material has survived, and there are surprisingly few detailed historical references to varnishing, but the best evidence is that artists throughout the history of oil and tempera painting employed varnish (Dunkerton et al., 1990). Some types of paintings, such as *tuchlein,* were not varnished, but few examples have survived. Court painters of the sixteenth and seventeenth centuries used varnish comprehensively, leading to the establishment of the first recorded varnish removal campaigns (Veliz, 1986). By the eighteenth and nineteenth centuries, when state academies controlled much professional painting practice, the need for a varnish became de rigeur. The concept of *finish* embodied many notions and became an unwritten contract of quality and reliability between academician and purchaser of art. It seems likely therefore that professional artists and their clients or patrons have always considered the application of varnish as a necessity of permanence and that artists have chosen to exploit its properties for both visual and practical benefit.

Many artists, through ignorance or untidy practice, continued painting up to exhibition deadlines and then immediately brushed varnish onto undried paint. Notoriously, J. M. W. Turner mixed soft-resin varnish, such as mastic, in his paint to improve its short-term handling properties and even continued painting after varnishing. Adding a soft natural resin to oil paint remained popular into the middle of the twentieth century (Doerner, 1934:156–160, 187–189). It provides a glossy surface but in quantity prevents the oil from becoming sufficiently cross-linked

to resist a solvent used to remove the varnish. Cleaning, then, has much to do with artist's painting practices and their consistency throughout a painting.

In the modern period the use of varnish has been questioned, at first as a reaction to the controlling academies and then as a challenge to the concept of permanence. The Impressionists realized that a yellow varnish would alter their high color tones and kill blue or purple shadows. With the center stage moving away from the academies the role of varnishing seems to have been left to commercial concerns. Dealers continued to apply varnish, even to Impressionist paintings (Swicklik, 1993) and to sellable sketches or unfinished works, which could be given a shiny finish. Increasingly, however, their clients came to value the creative process as part of a change in perception and philosophy, particularly to encompass the constantly changing industrial nature of the world. Much of modern art explores creativity and originality, and this does not sit well with the notion of finish or, indeed, longevity (Learner, 2000). Closer to home, we might recognize the museum replacing the academy as the ultimate arbiter of taste and taking over from the patron as the champion of permanence. What is clear is that we cannot now assume a consensus on the old certainties of what a work of art is for, how long it should last, and how it should be presented.

These are huge philosophical issues that conservators cannot be expected to consider on their own (Mancusi-Ungaro, 1990). Yet, increasingly, the context of conservation is left undefined; the assumption is that the conservator gets to work and efficiently removes the material that obscures our view of the work, thereby revealing the genius of the artist. When this succeeds, the conservator shares some of the appreciation that is due to the artist, and when it disappoints, the conservator may feel a sense of failure. Of course, removing a darkened amber filter from a colorful painting can be dramatic, yet it is an act of faith that much of the subtle relationships will be improved by cleaning. These can rarely be judged through the darkened varnish.

Annual spring cleaning can simply be a matter of brushing or vacuuming dust from a varnish. Washing with water is more effective and may need to be done every decade or two. This normally requires a wetting agent to ensure good contact with the varnish surface and to trap dirt within the surface of the liquid. Traditional recipes including potatoes and onions are well known (Sitwell and Staniforth, 1998). Saliva is still considered effective, and many other materials have been recommended, including borax and urine. The top 10 μm of a varnish are most susceptible to UV radiation, air pollution, and moisture, and as the varnish ages, it becomes more polar and brittle and more soluble in aqueous mixtures. The varnish surface and, eventually, the body of the varnish disintegrate under the action of repetitive cleaning. Wax or poppy oil coatings can be applied to "feed" the varnish surface to extend its life, but opacity and yellowing destroy its optical qualities. Perhaps two generations will have passed since anyone saw the painting through a clear fresh varnish.

The removal of a well-oxidized mastic varnish from a thoroughly dried oil film (Percival-Prescott, 1990) using, for example, spirits of wine has been carried out for centuries (Caley, 1990). The alternative of using abrasion to break up the friable mastic film has also been a long-standing mainstay of cleaning paintings. It was in the eighteenth century that artists began to modify their mediums by the addition of varnishes and waxes. In combination with the introduction of oil varnishes and the retouching of damage using oil paint the job of the restorer became much more difficult (Carlyle, 1990). Unwanted oil had to be broken down without damaging original paint using chemical means. Saponification or alkaline hydrolysis was the method available, typically achieved by the use of lye soap or pot ash. Then, as now, the problem of controlling the reaction on the surface of the painting provided a considerable challenge. Alkaline material must be confined to the area to be broken down and then removed or neutralized to prevent further reaction without spreading it onto delicate original paint. Evaporative ammonium hydroxide–based formulas have found favor. The removal of tough old oil films can also be helped by applying mechanical methods of scraping or lifting with a scalpel, sometimes combining reagent, solvent, and scalpel methods iteratively to deplete the overpaint. The process requires great skill, concentration, and effort, with the recognition that the room to maneuver is minimal and that any slip is likely to cause damage.

Solvents have been, and frequently remain, the first choice for conservators for removing a varnish. Traditionally, spirits of wine and turpentine have been the most readily available solvents since distillation was brought to Europe. Essential oils such as lavender, rosemary, cloves, and many others were also available as restrainers. In the nineteenth century, more specific chemicals became available.

Ruhemann (1968:270) described the margin test, which involves using very small swabs to check each area and confine any potential damage at the level of visual resolution. Stolow (1956) measured the swelling of paint films by organic solvents, providing the first framework in which to compare our choice of solvents (Feller et al., 1959). Stolow's interpretation met with criticism from practitioners, who realized that it distorted the model of the cleaning process by ignoring rates of solvent evaporation, which are used to control exposure during evaporative swab cleaning. More recently, Phenix (2002) has raised new concerns about this research. For progress to come from scientific research, projects need to be well informed by practitioners in order to address the right questions, and researchers need to translate their results into the conservators' studio practice (Ormsby et al., 2007). The next step is to report back to the scientist the practical experience of any new method in order to refine the analysis and repeat the cycle.

The Teas (1968) diagram was the first three-dimensional map of solubility, providing a better theoretical framework (Hedley, 1980), but as Feller pointed out, a map does not tell you where you are, it is only useful when you have located your position. There is still much more to learn about the drying of oil paints and the behavior of dried linoxyn films (Mecklenburg and Tumosa, 1991); the interaction of oil with pigments (Keune

et al., 2005) and natural resins; the behavior of these systems on subsequent oxidation and deterioration (Erhardt and Tsang, 1990) and how all this affects the swelling of paint by solvents (Hedley et al., 1990) and water (Michalski, 1990).

Alternatives to solvents have been championed by Wolbers (1988), who has proposed a new approach to cleaning paint surfaces and has put into place a theoretical framework to give his suggestions credibility. The careful selection of appropriate surface active agents in water-based systems can be effective in removing oxidized varnishes and oil varnishes as well as dirt. Initial concern was centered on doubts about the effective clearance of nonevaporating high molecular weight material, but these concerns have largely been addressed (Khandekar, 2000). Wolbers' formulations have provided new tools to remove stubborn material more controllably.

Unvarnished paintings are a relatively new challenge to conservators. During the 1970s a group of unfinished Turner oil sketches were cleaned at Tate (Williams, 1989). An interesting group, they had over 120 years of dirt accumulation since they left the artist's dirty studio (Phenix and Burnstock, 1990). In some cases the tentative sketches could not be seen through the dirt. Various water-based cleaning methods were tried, such as saliva, dilute ammonium hydroxide, and nonionic detergents. All removed much of the dirt layer but left an uneven gray on the predominant white absorbent ground. The problem was how to pick up the residual gray layer. The solution chosen was to use a plasticized polyvinylchloride eraser (Mars Staedtler) through a water-wetted surface. The dirt was incorporated into the eraser and removed from the absorbent surface (Hackney, 1990). Later, triammonium citrate was tried on similar material and found to produce the same result. It acted as a chelating agent, latching onto molecules associated with the dirt particles (Carlyle et al., 1990). Wolbers (2000) explains why lead was detectable on cleaning swabs.

Textile and paper elements are frequently exposed on modern works of art. These are absorbent surfaces with hydroxyl groups that readily attach to particles, drawing dirt in with capillary forces and trapping it mechanically in its open fibrous structure. Wet cleaning methods can be effective at dirt removal but can dramatically change the surface texture and appearance. Dry cleaning with powders is less effective, even with bread, where some moisture is present and largely bound to the bread. A combination of gentle abrasion and dirt pick up leaves the overall surface cleaner and intact but is not sufficient to deal with localized stains. Various suction systems devised for paper and textile conservation can be applied locally.

Whether removing dirt or varnish, there are many examples of conservators using ingenuity, borrowing from other disciplines, extrapolating from traditional methods, or just intelligently employing a repertoire of established techniques. But when working on individual paintings, assessing the results can be difficult and rarely allows true comparison with alternative methods. Scientific studies can better do this job of explaining observed successes and analyzing mechanisms.

More detailed examination using cross sections or increasingly sophisticated analysis can reveal the construction of the paint and varnish layers (Mills and White, 1987). This can tell a conservator how much dirt is on the surface or under the varnish and where any original glazes sit in the paint layer and reveal evidence of retouching. It may also identify a very thin layer of glair varnish (Peres, 1990) or one that gives the paint film a patina (Philipott, 1966). Ultraviolet fluorescence identifies the extent of varnish and earlier retouching, and local cleaning tests reveal the varnish solubility and localized response of the paint to solvents. A knowledge of artists' methods derived from the study of other paintings as well as an interpretation (Brandi, 1949) of the painting being cleaned is important prior knowledge, a mental model of what is expected, allowing a more detailed investigation of the work in question. Materials analysis can reveal the pigments and main medium, and increasingly, it is possible to detect minor components, such as the all-important additives to the medium, which can change its properties significantly.

CURRENT SITUATION

In recent years there have been many studies of artists' materials and techniques, in part to understand an artist's intention but also to assist with a conservation treatment. It is essential to know how consistent an artist is in the use of materials, for example, the addition of varnish or wax to paint to improve its handling or dried properties; reworking an area; scraping down paint; overpainting; painting wet on wet; leaving the work for a long period during painting; using novel application methods, such as palette knife, spray gun, collage, or frottage techniques; creating texture by the addition of coarse material or the extraction of oil medium to form an absorbent surface; combining different media either in layers on the painting or premixed on the palette; or using poorly bound pigments. The possibilities are endless, and knowledge of the existence and location of all such potential problems is important to the conservator, helping to prevent misreading of the artist's intention and to distinguish between original and later material. It is the conservator's duty to understand the artist's normal range of practices and to examine the painting to develop a model of what the artist might have done. If the resources are available, and increasingly they are being demanded, some analysis can be made to address the questions raised by the conservator's examination (Hagan, 2007). Informed with this knowledge the conservator makes predictions on how the varnish and paint will respond to the chosen cleaning method and can gradually explore the painting surface.

REFERENCES

Brandi, C. 1949. The Cleaning of Paintings in Relation to Patina, Varnish and Glazes. *Burlington Magazine*, 91:183–188.

Caley, T. 1990. "Aspects of Varnish and the Cleaning of Oil Paintings before 1700." In *Cleaning, Retouching and Coatings: Preprints of the IIC Brussels Con-*

gress, ed. J. S. Mills and P. Smith, pp. 70–72. London: International Institute for Conservation.

Carlyle, L. 1990. "British Nineteenth Century Oil Painting Instruction Books: A Survey of Their Recommendations for Vehicles, Varnishes and Methods of Paint Application." In *Cleaning, Retouching and Coatings: Preprints of the IIC Brussels Congress*, ed. J. S. Mills and P. Smith, pp. 76–80. London: International Institute for Conservation.

Carlyle, L., J. H. Townsend, and S. Hackney. 1990. "Triammonium Citrate: An Investigation into Its Application for Surface Cleaning." In *Dirt and Pictures Separated,* ed. V. Todd, pp. 44–48. London: United Kingdom Institute for Conservation.

Doerner, M. 1934. *The Materials of the Artist and Their Use in Painting*. New York: Harcourt, Brace.

Dunkerton, J., J. Kirby, and R. White. 1990. "Varnish and Early Italian Tempera Paintings." In *Cleaning, Retouching and Coatings: Preprints of the IIC Brussels Congress*, ed. J. S. Mills and P. Smith, pp. 63–69. London: International Institute for Conservation.

Erhardt, D., and J. Tsang. 1990. "The Extractable Components of Oil Paint Films." In *Cleaning, Retouching and Coatings*. Preprints of the IIC Brussels Congress, ed. J. S. Mills and P. Smith, pp. 93–97. London: International Institute for Conservation.

Feller, R. L., N. Stolow, and E. H. Jones. 1959. *On Picture Varnishes and Their Solvents*. Oberlin, Ohio: Intermuseum Conservation Association.

Gombrich, E. 1962. Dark Varnishes: Variations on a Theme from Pliny. *Burlington Magazine,* 104:51–55.

Hackney, S. 1990. "The Removal of Dirt from Turner's Unvarnished Oil Sketches." In *Dirt and Pictures Separated,* ed. V. Todd, pp. 35–39. London: United Kingdom Institute for Conservation.

Hagan, E., M. Charalambides, T. Learner, A. Murray, and C. Young. 2007. "Factors Affecting the Mechanical Properties of Modern Paints." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. Kreuger, and M. Schilling, pp. 227–235. Los Angeles: The Getty Conservation Institute.

Hedley, G. 1980. "Solubility Parameters and Varnish Removal: A Survey." *The Conservator,* 4:12–18. Reprinted in *Measured Opinions: Collected Papers on the Conservation of Paintings*, ed. C. Villers, pp. 128–134. London: United Kingdom Institute for Conservation.

———. 1993. "On Humanism, Aesthetics and the Cleaning of Paintings." In *Measured Opinions: Collected Papers on the Conservation of Paintings*, ed. C. Villers, pp. 167–171. London: United Kingdom Institute for Conservation.

Hedley, G., M. Odlyha, A. Burnstock, J. Tillinghast, and C. Husband. 1990. "A Study of the Mechanical and Surface Properties of Oil Paint Films Treated with Organic Solvents and Water." In *Cleaning, Retouching and Coatings: Preprints of the IIC Brussels Congress*, ed. J. S. Mills and P. Smith, pp. 98–105. London: International Institute for Conservation.

Keune, K., E. Ferreira, and J. Boon. 2005. "Characterization and Localization of the Oil Binding Medium in Paint Cross-Sections Using Imaging Secondary Ion Mass Spectrometry." In *Preprints 14th ICOM-CC Triennial Meeting, The Hague,* ed. I. Verger, pp. 796–802. London: James and James.

Khandekar, N. 2000. A Survey of the Literature Relating to the Development of Aqueous Gel Cleaning on Painted and Varnished Surfaces. *Reviews in Conservation*, 1:10–20.

Learner, T. 2000. A Review of Synthetic Binding Media in Twentieth-Century Paints. *The Conservator,* 24:96–103. http://dx.doi.org/10.1080/01410096.2000.9995156.

Mancusi-Ungaro, C. 1990. "The Rothko Chapel: Treatment of the Black-Form Triptychs." In *Cleaning, Retouching and Coatings: Preprints of the IIC Brussels Congress*, ed. J. S. Mills and P. Smith, pp. 126–130. London: International Institute for Conservation.

Mecklenburg, M .F. and S. T. Tumosa. 1991. "An Introduction to the Mechanical Behavior of Paintings under Rapid loading Conditions," in *Art in Transit: Studies in the Transport of Paintings,* ed. M. F. Mecklenburg, pp. 137–173. Washington, D. C.: National Gallery of Art.

Michalski, S. 1990. "A Physical Model of Varnish Removal from Oil Paint." In *Cleaning, Retouching and Coatings: Preprints of the IIC Brussels Congress,* ed. J. S. Mills and P. Smith, pp. 85–92. London: International Institute for Conservation.

Mills, J., and R. White. 1987. *The Organic Chemistry of Objects*. London: Butterworths.

Ormsby, B., and T. Learner. 2009. The Effects of Wet Surface Cleaning Treatments on Acrylic Artists' Paints—A Review of Recent Scientific Research. *Reviews in Conservation,* 10:29–42.

Ormsby, B., P. Smithen, and T. Learner. 2007. "Translating Research into Practice—Evaluating the Surface Cleaning Treatment of an Acrylic Emulsion Painting by Jeremy Moon." In *Contemporary Collections: Preprints of the AICCM National Conference Brisbane*, ed. A. Pagliarino and G. Osmond, pp. 97–109, Canberra: Australian Institute for the Conservation of Cultural Materials.

Percival-Prescott, W. 1990. "Eastlake Revisited: Some Milestones on the Road to Ruin." In *Cleaning, Retouching and Coatings*. Preprints of the IIC Brussels Congress, ed. J. S. Mills and P. Smith, pp. 73–75. London: International Institute for Conservation.

Peres, C. 1990. "Vincent van Gogh's Triptych of Trees in Blossom, Arles (1888). Part II. On Egg White Varnishes." In *Cleaning, Retouching and Coatings:* Preprints of the IIC Brussels Congress, ed. J. S. Mills and P. Smith, pp. 131–133. London: International Institute for Conservation.

Phenix, A. 2002. The Swelling of Artists' Paints by Organic Solvents and the Cleaning of Paintings: Recent Perspectives, Future Direction. *Postprints (American Institute for Conservation of Historic and Artistic Works. Paintings Specialty Group)*, 15:71–86.

Phenix, A., and A. Burnstock, 1990. "The Deposition of Dirt: A Review of the Literature with Scanning Electron Microscope Studies of Dirt on Selected Paintings." In *Dirt and Pictures Separated,* ed. V. Todd. pp. 11–18. London: United Kingdom Institute for Conservation.

Phenix, A., and K. Sutherland. 2001. The Cleaning of Paintings: Effects of Organic Solvents on Oil Paint Films. *Reviews in Conservation,* 2:47–60.

Philipott, P. 1966. La notion de patine et nettoyage des peintures. *Bulletin de l'Institut Royal du Patrimoine Artistique*, 9:138.

Rees Jones, S. 1962. Science and the Art of Picture Cleaning. *The Burlington Magazine,* 104:61.

Ruhemann, H. 1968. *The Cleaning of Paintings*. London: Faber and Faber.

Sitwell, C., and S. Staniforth, eds.1998. *Studies in the History of Painting Restoration*. London: Archetype Press in association with the National Trust.

Stolow, N. 1956. Some Investigations of the Action of Solvents on Drying Oil Films. Ph.D. thesis, University of London, London, U. K.

Swicklik, M. 1993. "French Painting and the Use of Varnish, 1750–1900." In *Conservation Research,* pp. 157–176. Studies in the History of Art Monograph Series II, No. 41. Washington, D.C.: National Gallery of Art.

Teas, J. P. 1968. The Graphic Analysis of Resin Solubilities. *Journal of Paint Technology*, 40(516):19–25.

Veliz, Z. 1986. *Artists' Techniques in Golden Age Spain*. Cambridge, Mass.: Cambridge University Press.

Walden, S. 1985. *The Ravished Image*. London: Weidenfield and Nicholson.

Williams, R. S. 1989. "Blooms, Blushes, Transferred Images and Mouldy Surfaces: What Are These Distracting Accretions on Art Works?" In *Proceedings of the 14th Annual IIC-CG Conference*, ed. J. G. Wellheiser, pp. 65–84. Ottawa: IIC-Canadian Group.

Wolbers, R. 1988. *Notes for Workshop on New Methods in the Cleaning of Paintings*. Marina del Rey, Calif.: The Getty Conservation Institute.

———. 2000. *Cleaning Painted Surfaces: Aqueous Methods*. London: Archetype.

Surface Cleaning of Paintings and Polychrome Objects in Italy: The Last 15 Years

Erminio Signorini

ABSTRACT. The developments of cleaning methods for paintings in Italy during the past 15 years are described. Restoration in Italy has been mostly practiced by private restorers, whose limited budgets can hardly afford a good preliminary diagnostic campaign. Public laboratories, such as those that belong to Soprintendenze or museums, still represent a small minority compared to the total number of restorers. Research for less toxic materials and a more reasonable and cautious use of the traditional ones, as well as a concern for informing restorers, began during the 1990s. Since then, about 4,000 technicians have been trained, and a number of different training courses have taken place in Italy as well as in other countries. Not all the participants were converted to a rational approach based on the execution of solubility tests, followed by a layer-by-layer action to reach the highest selectivity, favoring aqueous methods whenever possible and using solvent-gelled processes rather than liquid ones to operate in the least invasive way. Nonetheless, a positive example of the increased sensitivity toward this methodological approach can be seen in the Restituzioni, an event that involves a series of restorations promoted by an important bank and that already has celebrated its 20th convocation. During the first years, a materials approach to the restoration of artifacts, such as canvases, panels, and painted sculptures, was more traditional, whereas after a decade, more and more interventions relied on the use of the solubility test, aqueous methods, gels, and other such approaches.

THE STARTING POINT

During the 1990s the awareness of methods and materials used for restoration in Italy was not very different from that of other European countries. To appreciate what little difference there was at that time, it is probably enough to compare the different reference texts on restoration used for training in Spain (Diaz Martos, 1974), France (Mâle, 1986), and, with some exceptions, Germany (Nicolaus, 1998).

At the time, the Italian literature on this subject was still not very precise or clear on how to approach cleaning during the treatment of a polychrome object. Even the most up-to-date texts of those years did not discuss this subject thoroughly. The most frequent suggestion given was to keep using the traditional methods that had been established mostly in Rome at the Istituto Centrale per il Restauro (Bon Valsassina, 1985; Bernini, 1988; Luciani, 1988). At best, the texts would offer suggestions on how to perform a good treatment, referring to a more specific bibliography (Perusini, 1989).

It cannot be ignored that quite often, Italian restorers would still find it difficult to step away from the precepts of old handbooks, such as that by Secco Suardo (1894), either in the original version or in its twentieth-century reprint edited by Gino Piva (1988). In 1989, a very important book that is still currently used for training in many

***Erminio Signorini**, Cesmar7—The Centre for the Study of Materials for Restoration, Via Mentana 5, 37128 Verona, Italy. Correspondence: erminio.signorini@gmail.com.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

Italian Conservation Schools was published, *La Chimica del Restauro* (Matteini and Moles, 1989). It is a very useful tool that discusses many materials used in the creation of artifacts, together with the materials commonly used during conservation treatments. Among these, cleaning materials are presented from a chemical and physical point of view; the way they work is explained, and the issue of their toxicity is also discussed. At the time of its first publication, this book systemized the knowledge and the practice of restoration, including cleaning. However, the Teas triangle diagram of solvents was only briefly mentioned and was still represented in an imprecise way.

THE STATE OF THE ART

In the second half of the twentieth century, the cleaning of easel paintings and polychrome objects in Italy was mainly performed with neutral organic solvents and acid and alkaline reactants, sometimes mixed together and/or with water. One of the most commonly used mixtures was obtained by mixing water with an alkaline substance in variable proportions.

The practice of cleaning was mainly based on a set of formulas and recipes considered effective to solve some problems such as removal of varnishes and retouchings; everything was entrusted to the practical skills of the restorer and his or her experience. Testing was performed with mixtures of different solvents that were ready in the studio for use and were considered efficient enough to remove ingrained surface dust rather than varnishes, unknown coatings on paintings, old retouchings, and old fillings. As reported in Table 1, each of those mixtures usually had an acronym as a name, made up of a number (the number of substances in the mixture) and letters (referring to the first letter of each substance).

This was obviously the common practice in private studios, whereas museums and studios belonging to the Soprintendenze could usually afford a good preliminary diagnostic campaign, which made it possible to avoid such empirical approaches. The Opificio delle Pietre Dure in Florence was the first institution to try and use a carrier or supporting material called a stearic emulsion, commonly known as *pappina fiorentina* (Matteini and Moles, 1984). This allowed a suspension of organic solvents and alkaline substances to be prepared in a very dense paste, thus avoiding their diffusion into the paint layers, and it proved to be much more efficient than the traditional methods relying on paper or cotton substrates.

Sometimes cellulose ethers were also employed as supporting materials for solvents. This was a common practice in cleaning frescos and stone artifacts, where a buffer mixture including a detergent and ethylendiaminetetraacetic acid (EDTA) in water, known as AB57, used carboxymethyl cellulose as the supporting material (Mora and Philippot, 1977; Colalucci, 1990).

Solvents with a high or medium level of toxicity were commonly used, e.g., butyl ammine, pyridine, carbon tetrachloride, and formic acid. It was also common practice to wash cleaned areas of the painting with liquid or gelled solvents. This operation was inappropriately called neutralization and was performed in order to eliminate any residue of the solvent or the acidic or alkaline substance previously employed during the cleaning process in order to halt its reaction. In practice, this practice only interfered with those solvents' evaporation time.

On the positive side, some very old methods, such as burning or regeneration of old varnishes, had gradually been abandoned. These methods were also quite risky for the health and safety of the restorer.

EARLY DEVELOPMENTS

The papers from the Brussels IIC Congress of 1990 (Mills and Smith, 1990) and other literature focusing on more updated

TABLE 1. Some common mixtures employed in restoration. Note that the acronyms stem from the Italian name of the solvents. DMF = dimethylformamide; n/a = not applicable.

Mixtures	Components	Ratio
2 A	water + ammonia	1:1
3 A	water + acetone + ethanol	1:1:1
4 A	water + ammonia + ethanol + acetone	1:1:1:1
AB	water + butylamine	1:1
ABD	water + butylamine + DMF	1:1:1
Benzine 80°C–100°C	Hydrocarbons	n/a
Nitro thinner	mixture of esters, ketones, alcohols, and aromatic hydrocarbons	variable, depending on the producer
DA	DMF + amyl acetate	1:1
DAN	DMF + amyl acetate + nitro thinner	1:1:1
DIDAX	DMF + synthetic thinner + xylol + acetone (35 + 15 + 10 + 10 mL, respectively)	3.5:1.5:1:1
Petroleum ether	Hydrocarbons	n/a
White spirit	Hydrocarbons	n/a

methods for cleaning paintings (Feller, 1972:9; Masscheleïn-Kleiner, 1991) only slowly gained acceptance in Italy, mainly because of the lack of an Italian translation for the papers. A good example would be the slow circulation that the Teas triangle diagram of solvents had in Italy in those years, although it had been employed in the conservation field as a starting point for solubility tests soon after its first inception in the 1960s.

At the time, the success of any conservation treatment was still pretty much delegated to the ability of the restorer to choose what to remove and what to keep on the painting in order to achieve a good result and restore its harmony and color balance. Sometimes this empirical approach was the reason that paintings exhibited blanching, salt formation on their surface as well as between original paint layers, dryness, and surface paint loss. Retouching and varnishing were considered a useful way to disguise these unwelcome effects.

The reasons why such risks were somehow considered impossible to avoid were briefly as follows:

- Any painting, after its treatment, had to look different from how it had looked before.
- A treatment had to be time efficient in order for the restorer to make the most of his or her time for both practical and economical reasons.
- Selectivity was not considered as any mixture of solvents was prepared with the aim of being as widely effective as possible.

These traditions from the past kept influencing restorers in Italy for a long time, even years after new solutions had been found. In fact, the literature in Italy also had already warned against those risks and suggested that caution be used with any solvent and that a painting could not always be transformed by cleaning. A layer by layer cleaning was always to be preferred.

A good example would be an excerpt from the essay *Breves Observaciones* by Poleró and Toledo (1868; published in Italian in 2010), who criticized excessive cleaning followed by excessive retouching, thus creating a painting sometimes completely different from the one intended by its creator. He stated (my translation), "An adequate cleaning is performed after reasoning on every single painting, in order to make the most of its beauty and enjoy the harmony of the color balance . . . finally to distinguish and recognize the hand of the original master."

THE TOXICITY ISSUE

Very similar behavior permeated the discussion on toxicity: a "good" restorer would know how long to use a toxic solvent and when to stop using it, without being affected by its use in any way. It was obviously not generally known for how long these toxic substances could remain in the environment and circulate within the human body, even after their use had been stopped or discontinued. At the time, no epidemiological analyses were carried out in this field that would have made these points clearer.

An ideal situation would have been a studio with good ventilation that also had a good extraction system, where the use of a toxic solvent, if safe for the object, could be controlled. Unfortunately, in private studios, the only protective items used, if any, were gloves and masks. Quite often, the situation was pretty much the same for studios belonging to institutions.

Toxicity eventually became a great concern in the 1990s, and it was the main reason for initiating the information campaign on new methods and techniques both in conservation schools and among restorers and conservators (Pietropolli, 2001). Thus, the search for less toxic materials and a more reasonable and cautious use of traditional ones (such as diethanolamine and hydrocarbons) were undertaken and are currently ongoing (Cremonesi et al., 2008; Cremonesi, 2009).

CLEANING

Quoting Secco Suardo (1894, reprinted 1988:317–318), "Let's listen to the history, let's talk with those men of art, and we will need to admit that more than time and more than wars and more than fires and iconoclasts, what really destroyed lots and lots of paintings is the ignorance of people pretending to clean them." There are similar words in many texts from the past. In individual small-sized enterprises, whose limited budgets can hardly afford a good preliminary diagnostic campaign, it is of fundamental importance to know tests and methods that every conservator can easily put into practice, for instance, the Feller solubility test, the Triansol software for calculating the solubility parameters a certain mixture of solvents (Bortolotti and Cremonesi, 1999), a newly proposed solubility test in Cremonesi and Signorini (2004), and so on.

OFFERING PROFESSIONAL DEVELOPMENT

Promoted by Paolo Cremonesi since 1995 and then by Cesmar7, the campaign to disseminate information on less toxic materials and more cautious techniques of cleaning paintings has involved so far about 4,000 restorers in Italy and hundreds in other countries. Training courses are both theoretical and practical and are usually organized as a basic course followed by an advanced one; both courses are usually taught by a chemist and a conservator. The same training is currently given in some conservation schools in Italy, whereas in other schools special workshops are given on these subjects.

The first time this updating campaign was presented in an international context was during the First International Congress "Colore e Conservazione" (Cremonesi, 2003a), held in Piazzola sul Brenta, near Padua, and organized by the Cesmar7 in 2002. At the same time, three workshops were organized by Cesmar7 and taught by Richard Wolbers to update cleaning methods and stimulate research, for example, on agar gels (Campani et al., 2007; Anzani et al., 2008), the use of cyclododecane as a

temporary protective coating in cleaning paintings (Hiby, 2008; Riggiardi, 2010), and water-based solutions for cleaning wax objects (Berzioli et al., 2010). Further workshops are currently in progress.

The restoration historian Bonsanti (2006:27) also has been involved in this movement, stating

> I have been following this campaign quite closely, and I am impressed by how quickly the new methods and materials spread among conservators and restorers . . . I am not saying that everybody in Italy is now converted to this rational approach, there are still difficulties sometimes in leaving the old habits and adopting the new proposed methods, mainly due to some inertia and technical difficulties found by some of the people operating in this field.

It is necessary to specify the following attitudes and actions among the people involved:

- Not everyone welcomed these new methods or was converted to this new approach.
- Some restorers decided to adopt only some of the solvents and recipes suggested.
- Others found it especially difficult to use water-based methods.

THE MOST SIGNIFICANT PROPOSALS

The main elements of this new approach are as follows:

- A rational and reasoned approach to cleaning should be used. Cleaning must be performed only after careful observation of the object that needs treatment and must be focused on solving any specific problems noticed. "The painting [is] a starting point," as Wishwa Raj Mehra (retired from Central Research Laboratory for Objects of Art and Sciences, Amsterdam, personal communication) has said.
- Tests should be used for water-based methods as well for solvent-based cleaning.
- Selectivity in choosing materials for cleaning as well as in using them is important. When possible, using gelled solvents rather than solvents in liquid form is suggested.
- The evaporation time of each solvent should be observed; the common practice of "washing" treated areas after cleaning should be avoided.
- Alternatives to toxic solvents and/or mixtures of solvents are preferred.

Some examples can be given. When this campaign first started, the high toxicity level of nitro diluents (a mixture of organic solvents, mainly toluene, acetone, dichloropropane, butyl cellosolve, isobutyl acetate, and isopropyl or isobutyl alcohol, in varying proportions depending on the dealer) and of butyl amine was clearly recognized. Dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and *n*-methylpyrrolidone were suggested instead because they are polar aprotic solvents with similar characteristics and solubility ability (Cremonesi, 2004). Concerns about their use came from their long retention time inside the paint layers and their very poor selectivity. These reasons were why employing them only if necessary was also suggested, with mixtures with more volatile solvents and/or in a gel preferred.

However, as a result of these suggestions, DMSO was soon adopted by many conservators and restorers as the "universal solvent" because of its capacity to quickly dissolve old varnishes and oil retouches as well as its lower toxicity. Alternatives to DMSO, even when possible, were not even considered, despite the fact that the use of dipentene, the racemic limonene, also had been suggested as a low- to medium-polarity solvent ($f_d = 75$, $f_p = 20$, where f_d and f_p are the Teas parameters characterizing the relative polar dispersion strength and hydrogen bonding, respectively) to replace some of the more toxic aromatic or chlorinated hydrocarbons or turpentine essence. Dipentene was considered a low-toxicity solvent, often found in soaps and other everyday products. However, further research and practical tests showed the risk of its polymerization: samples kept in jars far from daylight turned into an orange, very viscous liquid. In addition, its low volatility and long retention time in the painting layers led to curtailment of its use, and restorers were warned not to use it anymore.

DISCOVERING WATER

With the goal of finding alternatives to the well-known and commonly accepted use of toxic solvents the most innovative solution regarded water-based cleaning methods already proposed at the start of the campaign. Following Wolbers's (2000) footsteps, the elaboration of some current Italian methodologies that focused on the effectiveness and selectivity of new materials began. These methodologies were considered a great tool for education about a layer-by-layer approach to cleaning so as to reach a high selectivity. This subject will be only briefly discussed since it has been discussed in detail in previous international contexts. For example, in the nineteenth century some texts, e.g., Pietro Edwards (see Tiozzo, 2000), Forni (1866), Secco Suardo (1894), and Poleró y Toledo (1868), had already mentioned the use of water for cleaning paintings (Perusini, 2010). These texts mainly suggested the use of common water for surface cleaning, followed by varnish removal if necessary.

Much has been learned since that time, and the chemical and physical characteristics of water, its power, and the associated risks are better understood. The pH values compatible with painting materials and the addition of chelating agents, soaps, and enzymes in order to reach a certain result (Cremonesi, 2003b) are also better understood.

Many conservators welcomed the use of water-based methods in their private studios, despite the greater complexity in preparation and use, and are now aware of the importance of a careful cleaning performed to remove what is on the varnish and

not the varnish itself. Whether or not to remove old varnishes and overpaint layers is a critical choice that cannot be left in the hands of a conservator alone. Respecting the painting in its history and materials should always be the aim of any conservator and curator.

Chelating agents, such as EDTA salts, were already known and employed in the restoration of frescos and stone artifacts. For paintings, the alternative use of a weaker chelating agent, such as citric acid salts, was suggested. Because of their disaggregating ability, chelating agents should always be used in low concentrations (less than 1%), as has been always recommended. However, some restorers preferred to use them in higher concentrations, even up to 20%, thus causing damage to the pictorial layers.

Gels were suggested to thicken water-based solutions, but with the caveat that this practice would need to be carefully avoided on particularly damaged paint layers. It is now possible to choose among different gelling materials with different characteristics and specificities, whereas in the past there was no specific knowledge about any of them, except for the abovementioned carboxymethyl cellulose in the AB57 mixture and some paint strippers. On the other hand, it was quite common for conservators and restorers to use various weight paper, cotton, cellulose pulp, clays, and stearic emulsion.

BETWEEN TRADITION AND INNOVATION: ONE EXAMPLE

A positive example of the increased sensitivity toward this methodological approach is the Restituzioni (Restitutions), a periodic and very relevant event. In 1989 an Italian bank started the Restituzioni to promote conservation treatments of objects, and now it has had its 14th meeting.

The work carried out by prestigious institutions such as the Opificio delle Pietre Dure and the Istituto Centrale per il Restauro is not as significant for this discussion since their conservation choices, i.e., which objects to treat and how to treat them, would not reflect choices made in the private sector. That is why Cesmar7 activities are better reflected in the Restituzioni. A catalog has been published for each of the 14 years of the Restituzioni, each one containing reports of the objects treated each year (Rigon, 1989–2000; Bertelli, 2002–2008).

For this study 164 reports have been analyzed: 101 on paintings, 37 on panels, 15 on polychrome objects on inorganic support, and 11 on painted wooden objects. All the studied works are artifacts of great importance by artists such as Bassano, Tintoretto, Veronese, Ribera, Vivarini, Palma, Luca Giordano, Tiepolo, Carpaccio, Lotto, Titian, and Pinturicchio.

Even now, reports are still being written by curators and art historians. Initially, these reports tended to emphasize the historical aspects of the objects and their conservation treatments without providing any specific detail on the technical aspects. Generally, there was no mention of the materials involved and those used for specific treatments, and quite often, cleaning was just mentioned and not discussed at all. For instance, cleaning would be described as "gradual and differentiated cleaning" or "delicate cleaning." Solvents were commonly quoted as "adequate," "appropriate," or "convenient" and were generally classified as "weak organic solvents." Solubility tests were commonly referred to as cleaning tests with the well-known old mixtures mentioned and mainly involved high-polarity solvents; the use of toxic solvents was accepted and not disguised. Except for one single initiative of the Galleria d'Arte Moderna in Milan carried out over the past two years, so far there have been no systematic studies on all the treatment reports stored in museums and Soprintendenze.

In 1996, things started to change. In that year's Restituzione catalogue (Rigon, 1996) a new attitude was evident. For the first time new materials were mentioned, such as artificial saliva, buffer solutions, water-based solutions, solvent gels, resin soaps, the Feller test, the new solubility test with LA-LE-AE (ligroin-acetone, ligroin-ethanol, acetone-ethanol), and so on.

Ten years later, Bonsanti, in the introduction of 2006 Restituzioni catalog, made a point about the positive diffusion of the new proposed methodologies and techniques, now commonly used in private studios as well as in those studios belonging to public institutions. At the same time, he admitted that old habits and techniques still existed in some places, proudly employed by renowned conservators and too often allowed by curators in charge of the conservation and protection of those works of art. It is clearly evident that an evolution, in both materials and techniques, is now in progress; it is not surprising, however, that this process is far from being completed. This increased sensibility toward a methodological approach is an integral part of a conservator's professional development.

CONCLUSIONS

The methodologies and techniques discussed here mainly apply to old artifacts and original historical materials. Further research is required in this field, and less invasive cleaning methods hopefully will be developed. More studies are necessary, especially for the field of contemporary art. The use of other methods, such as rubbers, needs to be evaluated, including the risks related to their use and the possible interactions they may have with other materials.

A field to explore is that of physics-based methods for cleaning. Research is the keyword, both for prevention and for conservation. There is plenty to be done by all professionals involved in various ways in the conservation field. This is why the conservation-restoration profession still has a fundamental meaning and many prospects and possibilities ahead.

Acknowledgments

I thank Paolo Cremonesi for collaboration over the years and for introducing me to the new cleaning methods. I also thank

Enrica Griseta for her support in the translation from the Italian and Fiorenza Redi for helping in the compilation of the text.

REFERENCES

Anzani, M., M. Cagna, E. Campani, A. Casoli, P. Cremonesi, M. Fratelli, A. Rabbolini, and D. Riggiardi. 2009. *Gel rigidi di agar per il tratamento di pulitura di manufatti in gesso*. [Use of Rigid Agar Gels for cleaning Plaster Objects.] Quaderno Cesmar7, No. 6. Padua: Il prato.

Bernini, D. 1988. *Laboratorio di restauro 2*. [Restoration Workshop 2.] Rome: Palombi Editore

Bertelli, C. ed. 2002–2008. *Cataloghi Restituzioni.* [Restitution CatalogsCatalogs Returns.] Vicenza, Italy: Banco Ambrosiano Veneto/Banca Intesa.

Berzioli, M., A. Casoli, P. Cremonesi, M. Fratelli, D. Riggiardi, and I. Zorzetti. 2010. *Verifica analitica dell'idoneità delle soluzioni acquose nella pulitura di sculture in cera*.[Analytical Verification of the Suitability of Aqueous Solutions in the Cleaning of Wax Sculptures.] Quaderni Cesmar7, No. 7. Padua: Il prato.

Bonsanti, G. 2006. "Restauro a colori." [Restoration in Color.] In *Cataloghi Restituzioni,* ed. C. Bertelli, p. 27. Vicenza, Italy: Banco Ambrosiano Veneto/Banca Intesa.

Bon Valsassina, C. 1985. *Laboratorio di restauro 1*. [Restoration Workshop 2.] Rome: Palombi Editore.

Bortolotti, I., and P. Cremonesi. 1999. Un approccio più scientifico alla pulitura dei dipinti. Triansol: Il Triangolo delle Solubilità, un software per il restauro. [A More Scientific Approach to the Cleaning of Paintings: Triansol, the Solubility Triangle, a Software for Restoration.] *Progetto Restauro*, 10:42–45.

Campani, E., A. Casoli, P. Cremonesi, I. Saccani, and E. Signorini. 2007. *L'uso di agarosio e agar per la preparazione di "gel rigidi*." Use of Agarose and Agar for Preparing "Rigid Gels." Translation by D. Kunzelman. Quaderni Cesmar7, No. 4. Padua: Il prato.

Colalucci, G.1990. *"Stato di conservazione" in Michelangelo e la Sistina. La tecnica, il restauro, il mito*. ["State of conservation" in Michelangelo and the Sistine. The technique, restoration and Myth.] Rome: Palombi Editore.

Cremonesi, P., ed. 2003a. *Materiali tradizionali ed innovativi nella pulitura dei dipinti e delle opere policrome mobili.* [Traditional and Innovative Materials in the Cleaning of Paintings and Polychrome Objects.] Padua: Il prato.

———. 2003b. *L'uso di tensioattivi e chelanti nella pulitura di opere policrome*. [The Use of Tensioactive and Chelating Agents in the Cleaning of Polychrome Objects.] I Talenti 10. Padua: Il prato.

———. 2004. *L'uso dei solventi organici nella pulitura di opere policrome.* [The Use of Organic Solvents in the Cleaning of Polychrome.] I Talenti 7. Padua: Il prato.

———. 2009. Parola d'ordine: ligroina! . . . Vale ancora? [Key Word: Ligroin! . . . Still appropriate?] *Progetto Restauro,* 51:38–47.

Cremonesi, P., and E. Signorini. 2004. L'uso dei solventi organici neutri nella pulitura dei dipinti: Un nuovo test di solubilità. [The Use of Organic Neutral Solvents in the Cleaning of Paintings: A New Solubility Test.] *Progetto Restauro,* 31:2–15.

Cremonesi, P., E. Signorini, I. Saccani, and L. Landi. 2008. DEA, la sorella cattiva della TEA. [DEA, the Bad Sister of TEA.] *Progetto Restauro,* 47:2–3.

Diaz Martos, A. 1974. *Restauración y conservación del Arte Pictorico*. [Restoration and Conservation of Pictorial Art.] Madrid: Arte Restauro.

Feller, R. L. 1972. "The Relative Solvent Power Needed to Remove Various Aged Solvent Type Coating." In *Paintings and the Graphic Arts*: *Preprints of the IIC Lisbon Congress,* ed. N. Brommelle and P. Smith, pp. 158–161. London: International Institute for Conservation.

Forni, U. 1866. *Manuale del pittore restauratore*. [Handbook for the Painting Restorer.] Florence: Le Monnier. Reprinted, Florence: Edifir, 2003.

Hiby, G., 2008 *Il Ciclododecano nel restauro di dipinti su tela e manufatti policromi*. [Cyclododecane in the Restoration of Paintings on Canvas and Polychrome Artifacts.] Quaderni Cesmar7 No.5. Padua: Il prato.

Luciani, R. 1988. *Il restauro*. [Restoration.] Rome: Palombi Editore.

Mâle, E. 1986. *Restauration des peintures de chevalet*. [Restoration of Easel Paintings.] 3rd ed. Fribourg, Switzerland: Office du Livre.

Masschelein-Kleiner, L. 1991. *Les solvents*. [Solvents.] Brussels: Institute Royal du Patrimoine Artistique.

Matteini, M., and A. Moles. 1984. *Scienza e Restauro*. [Science and Restoration.] Florence: Nardini.

———. 1989. *La chimica nel restauro: I materiali dell'arte pittorica*. [Chemistry in Conservation: The Materials of Paintings.] Florence: Nardini.

Mills, J. S., and P. Smith, eds. 1990. *Cleaning, Retouching and Coatings: Technology and Practice for Easel Paintings and Polychrome Sculpture*: *Preprints of the IIC Brussels Congress*. London: International Institute for Conservation.

Mora, L., and P. Philippot. 1977. *La conservation de Peintures Murales*. [The Conservation of Mural Paintings.] Bologna: Compositori.

Nicolaus, K. 1998. *Handbuch der Gemälderestaurierung.* Cologne: Könemann. [Italian translation published as *Il restauro dei dipinti*. Cologne: Könemann, 2001.]

Perusini, G. 1989. *Il restauro dei dipinti e delle sculture lignee*. [Restoration of Paintings and Wooden Sculptures.] Udine, Italy: Del Bianco.

———. 2010. "L'arte de la Restauración di Poleró y Toledo (1853) e alcuni trattati di restauro europei del XIX secolo." In *L'Arte del Restauro*, ed. E. Signorini, pp. 17–34. Padua: Il prato.

Pietropolli, A., ed. 2001. *Salute e Restauro*. Quaderni di Progetto Restauro 3. Padova: Il prato.

Piva, G., ed. 1988. *L'arte del restauro*. [The Art of Restoration.] Milan: Hoepli.

Poleró y Toledo, V. (1868) *Breves observaciones sobre la utilidad y conveniencia de reunir en uno sólo los dos museos de pintura de Madrid, y sobre el verdadero estado de conservación de los cuadros que constituyen el Museo del Prado*. [Brief Observations on the Convenience of Uniting Both Painting Museums of Madrid and on the True State of Conservation of the Paintings that Constitute the Prado Museum.] Madrid: Eduardo Cuesta. [Italian translation published as "Brevi osservazioni, sull'opportunità di riunire in uno solo i due musei di pittura di Madrid e sul reale stato di conservazione dei quadri del Museo del Prado." In *L'arte del restauro*, ed. E. Signorini, pp. 37–40. Padua: Il prato, 2010.

Riggiardi D., ed. 2010. *Il ciclododecano nel restauro dei manufatti artistici*. [Cyclododecane in the Restoration of Works of Art.] Quaderni Cesmar7, No. 8. Padua: Il prato.

Rigon, F. ed. 1996. *Cataloghi Restituzioni.* [Catalogs Returns.] Vicenza, Italy: Banco Ambrosiano Veneto/Banca Intesa.

Secco Suardo, G. 1894. *Il restauratore di dipinti*. [The Restorer of Paintings.] Milan: Hoepli. Reprinted, Milan: Cisalpino Goliardica, 1988.

Tiozzo, V., ed. 2000. *Dal decalogo Edwards alla Carta del restauro—Pratiche e principi del restauro dei dipinti*. [From the Edwards Decalogue to the Restoration Charter—Practice and Principles of Painting Restoration.] Padua: Il prato.

Wolbers, R. 2000. *Cleaning Painted Surfaces*: *Aqueous Methods*. London: Archetype Publications. [Italian translation published as *La pulitura di superfici dipinte: Metodi acquosi*. Padua: Il prato, 2005.]

Extended Abstract—A Preliminary Investigation into the Surface Characteristics of Paint and the Implications for Restoration

Laurent Sozzani

INTRODUCTION

This study presents an initial investigation into the surface characteristics of the uppermost paint layer of paintings, i.e., the finished final paint surface. The primary focus is on how to characterize differences in surface morphology between intact and damaged paint in order to understand how small local disruptions (primarily abrasion) at the very surface of otherwise intact paint affect the overall visual impression of a painting. To what extent does surface abrasion or the additive effect of small areas of surface abrasion interfere with our reading of the picture? When viewing a painting, a broad spectrum of the surface phenomena contributes to our perception (natural aging, such as color fading and shifts in color, discolored varnish, cracks, results of restorations, etc.).

To better understand this phenomenon, differences between intact and abraded surface areas of the same paint layer were examined using a variety of analytical techniques (Figure 1). Gross abrasion that exposes distinctly different lower paint layers was not considered. A way was sought to record subtle visual differences and to qualify and quantify them, with the goal of using this information in restoration strategies.

PROCEDURE

A study of paint samples was undertaken to identify the morphological and physical characteristics of the surface before and after cleaning, with and without an intentional abrading. Various analytical means were used to study surface morphology, such as digital photography, colorimetric studies, roughness measurements (confocal white light profilometry), and microscopic observation, both stereoscopic and scanning electron microscopy (SEM). These were used to evaluate and categorize characteristics that contribute to our perception of a painting (Figure 2).

IMPLICATIONS IN THE RESTORATION OF PAINTINGS

Does the damaged surface of what, on first appearance, may seem to be an intact paint differ visually from an otherwise undamaged paint? Can the analysis of surface

***Laurent Sozzani**, Paintings Restoration Department, Rijksmuseum, Amsterdam, Postbus 74888, Amsterdam, The Netherlands. Correspondence: l.sozzani@planet.nl.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

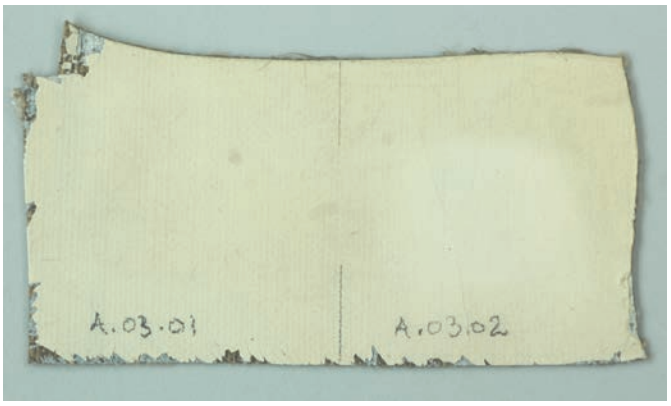


FIGURE 1. Sample of slightly aged lead white paint. Note that the surface of (left) the unabraded area is visually darker than (right) the abraded area.

phenomena of a paint film have a direct effect on the direction of a painting restoration? As is the case with a collection of visual effects, even subtle disturbances to the surface can and do alter its character. The restoration of a painting often includes the restoration of missing paint in order to reestablish the original, albeit aged, appearance of the composition.

Controversy as to the extent to which a restoration can or should be carried out can be found in almost every discussion on the subject (Walden, 1985; Bomford, 1994; Garland, 2003; Bomford et al., 2004). Although retouching actual paint loss (including glaze layers) and abraded paint that exposes underlying color is widely accepted in the practice of painting restoration, retouching or "toning" to restore only the damaged surface of otherwise intact paint is more often questioned. Observing what constitutes the surface of a painting and to what extent subtle disturbances play a role in the actual appearance of a painting may aid in understanding to what extent subtle damage plays a role in the actual appearance of a painting and also add insight into treatment options.

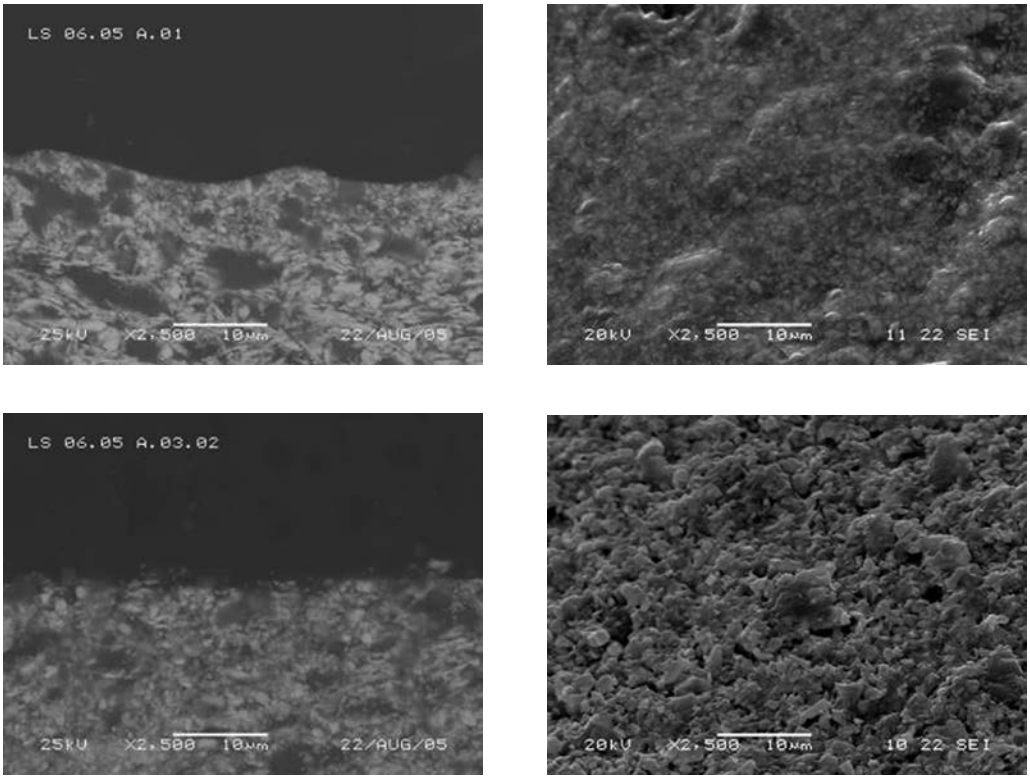


FIGURE 2. The SEM micrographs show (left) the cross section and (right) the surface of the samples. The micrographs on top show the unabraded paint, and those below show the abraded one. In the cross sections, the once smooth surface (top) is, after abrasion, jagged with loose pigment particles (bottom). The surface, smooth and closed before abrasion (top), becomes open and porous in the abraded paint (bottom). In an older painting the medium would be naturally oxidized and discolored. The absence of medium and the open exposed pigment particles could result in shifting the color away from the surrounding more intact paint.

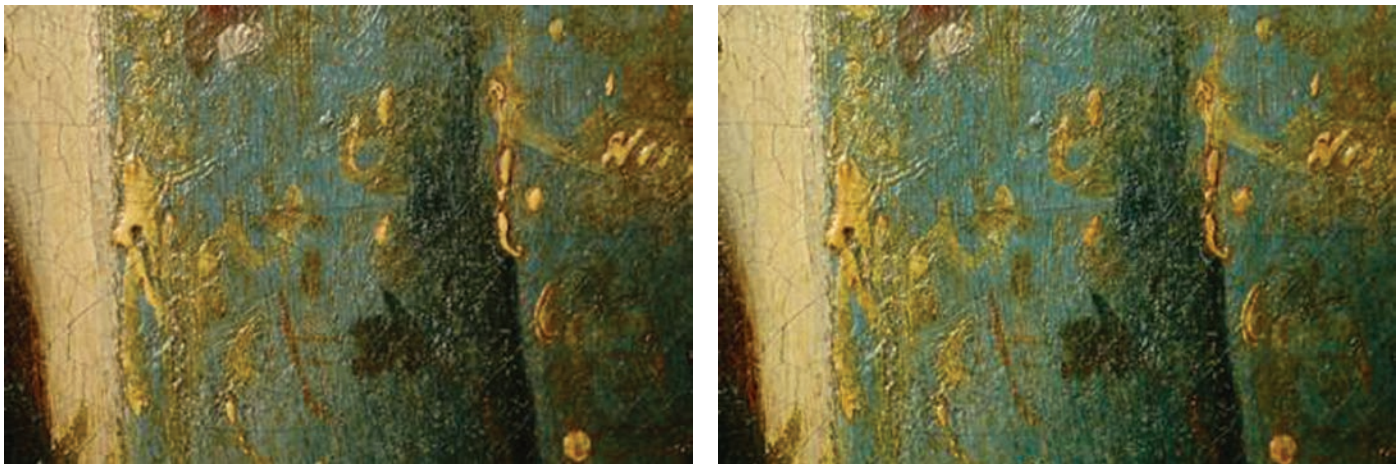


FIGURE 3. Detail of a painting after cleaning, (left) before retouching and (right) after retouching. Note the small highlights that are abraded reveal the pure color of the original bright yellow paint that is now in high contrast with the surrounding lower key unabraded paint, which has a natural aged tone. The bright yellow highlights can actually have a disruptive effect on the composition. Minimal retouching and slightly toning the bright spots will harmonize the passage and re-establish form and volume.

SUMMARY OF RESULTS

Abrasions through the surface of naturally aged discolored paint, such as lead white, lead tin yellow, or copper resinate green, can often be readily observed as points or areas of bright color, usually located on the peaks of impasto. The bright area is then surrounded by aged, less colorful paint (Figure 3).

Once familiar with this type of abrasion where contrast is high, a restorer can recognize more subtle shifts in color in broader planes of seemingly intact paint. The contrast, which can be dramatic, can be instructive in understanding the original use of color by the artist; however, it can also have a disruptive effect on the composition. Microanalysis confirms that the color shift is indeed the result of differences in surface structure between undamaged and damaged paint. Carefully retouching such actual damage to the paint surface, with only a slight wisp of retouching paint to eliminate the visual disturbances, can have a considerable effect in unifying the overall appearance of the picture. Identifying, acknowledging, and restoring damage to the naturally aged paint can reintegrate and visually harmonize abraded color passages, resulting in a subtle yet recognizable aesthetic impact on the overall composition that in no way compromises the artist's original intention, but rather reestablishes it.

Acknowledgments

The author thanks W. Wei, Institute Collectie Nederlands (ICN), for his help with confocal white light profilometry and both K. Mench, Shell Laboratories Amsterdam, and I. Joosten, ICN, Amsterdam, for SEM examinations. Thanks also go to Dorothy Mahon at The Metropolitan Museum who, once upon a time, long ago, pointed out to me abraded impasto on a "perfectly preserved" Martin Johnson Heade painting.

REFERENCES

Bomford, D. 1994. "Changing Taste in Restoration of Paintings." In *Restoration: Is It Acceptable?*, ed. A. Oddy, pp. 33–40. British Museum Occasional Papers 99. London: British Museum.

Bomford, D., and M. Leonard, eds. 2004. *Issues in the Conservation of Paintings*. Readings in Conservation. Los Angeles: Getty Publications.

Garland, P., ed. 2003. *Early Italian Paintings: Approaches to Conservation: Proceedings of a Symposium at Yale University Art Gallery*. New Haven, Conn.: Yale University Art Gallery.

Walden, S. 1985. *The Ravished Image: Or How to Ruin Masterpieces by Restoration*. New York: St. Martin's Press.

Extended Abstract—Noncontact and Noninvasive Monitoring of Overpaint Removal with Optical Coherence Tomography

Magdalena Iwanicka, Dagmara Kończalska, Piotr Targowski, and Bogumiła J. Rouba

INTRODUCTION

Optical coherence tomography (OCT) is a noncontact and noninvasive technique of depth-resolved structural imaging within media that moderately scatter and/or absorb near-infrared light. It originates from diagnostic medicine and has been under consideration for examining art objects since 2003. A fairly complete list of papers on application of OCT to examination of artworks may be found on the Web (http://www.oct4art.eu).

The technique uses low-coherence interferometry; therefore, the light source must be characterized by low temporal (to ensure high axial resolution) and high spatial coherence. The instrument used in the study had a superluminescent diode as a light source, with an 845 nm central wavelength and a 107 nm bandwidth, resulting in a 4.5 μm axial resolution in air (3 μm in varnish). The spectral domain modality of the technique was chosen to ensure high sensitivity (over 100 dB) and speed of data acquisition. The modular construction based on fiber optics makes it fairly portable, and thus, it does not require optical table mounting. The system's portability together with fast and straightforward data acquisition makes OCT particularly well suited for quick evaluation of conservation treatment (Liang et al., 2008).

The results obtained by means of this method are presented in a convenient manner of cross-sectional images (called B-scans in analogy to ultrasonography) that are easy to compare with conventional microscopic stratigraphy analysis. The advantage of OCT lies not only in its noninvasiveness but also in its ability to examine a relatively wide area. The described instrument provides B-scans of 15 mm width and 2 mm depth. Additional scanning in the perpendicular direction gives 3-D information about the spatial structure of the sample. Because of the high speed of data acquisition, the tomograph is capable of 3-D (volume) data collection within seconds. The obvious disadvantage of the method is that the imaging is limited to media at least partially transparent to infrared light (Szkulmowska et al., 2007). Therefore, OCT is mostly used for examination of transparent and semitransparent structures, such as varnishes and glazes on easel paintings. It is, however, possible to resolve the thickness and structure of these layers noninvasively in as many places as desired. If the axial resolution permits, the superimposed layers of different varnishes, retouches, and primary layers can be differentiated. The method may also be used for identification of the location of certain pigmented layers within the varnish-glaze structure. In this contribution, the applicability of OCT to monitor the removal of secondary strata is shown, using an eighteenth-century painting as an example.

***Magdalena Iwanicka**, **Dagmara Kończalska**, and **Bogumiła J. Rouba**, Institute for the Study, Restoration and Conservation of Cultural Heritage, Nicolaus Copernicus University, Gagarina 7, 87-100 Toruń, Poland. **Piotr Targowski**, Institute of Physics, Nicolaus Copernicus University, Grudziądzka 5, 87-100 Toruń, Poland. Correspondence: Magdalena Iwanicka, magiwani@gmail.com.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

APPLICATION EXAMPLE

The picture depicting Saint Leonardus of Porto Maurizio was executed probably soon after Leonardus's beatification in the year 1797. However, after he had been proclaimed a saint in 1867, the painting was altered in order to reflect Leonardus's new status: the nimbus was added, as well as a secondary inscription, "St. Leonard." At the same time the primary inscription was overpainted together with the whole background area. The exact location of both inscriptions within the painting's structure was resolved by means of optical coherence tomography and is described elsewhere (Targowski et al., 2010).

This study focuses on the application of optical coherence tomography to resolve the problems that emerged during the conservation of the painting. The overpaint was lying on three to four layers of varnish. It was decided that the overpaint would be removed while attempting to preserve the old varnishes underneath. Since, as the result of this treatment, the primary inscription was to be revealed, the aim of the research was to find the most safe and satisfactory treatment procedure. Cross-sectional views (OCT B-scans) were used both to assess noninvasively the integrity of the primary layers covered by the overpaint (Figure 1, left-hand side of the OCT images) and to examine the condition and thickness of these layers revealed as a result of the overpaint removal (Figure 1, right-hand side of the images).

During the first stage of the experiment, small trials of overpaint removal were performed with different solvent compositions in the background area of the painting. The results were evaluated with OCT. The composition of isopropanol, water, and ammonium (9:1:1) applied with cotton swabs gave the most satisfactory and even results: the overpaint was removed completely, and the varnishes were preserved. However, further overpaint removal on the larger areas of the background proved less successful. OCT cross-sectional images revealed little holes in the varnish layer, which had started to occur before the overpainting was removed completely. Therefore, another set of OCT monitored trials was performed in order to evaluate the effect of using the same solvent composition, but with different removal procedures, such as rolling with a cotton swab, brushing, exposing to poultices, removing mechanically with a scalpel, and

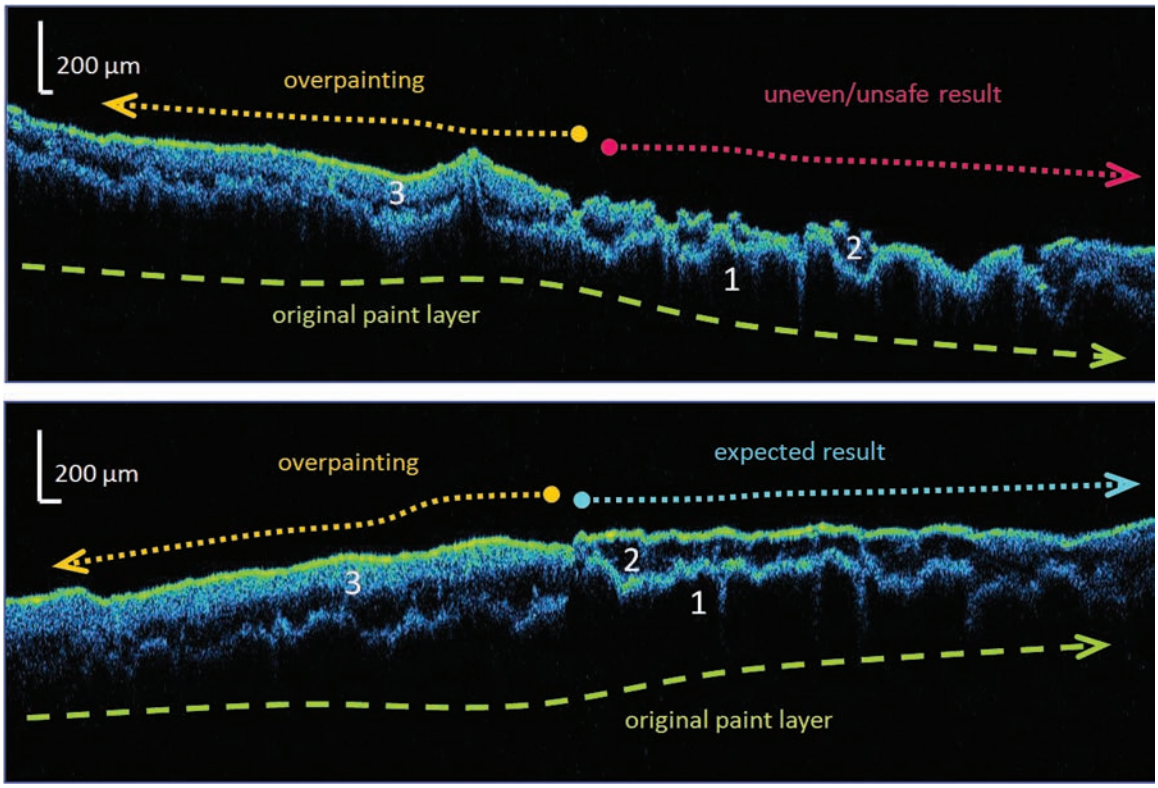


FIGURE 1. Trials of overpaint removal with different solvent compositions with the results evaluated by means of OCT. Consecutive layers are visible in the OCT tomograms: 1, original paint layer; 2, three to four layers of varnish; 3, overpaint layer. (top) Poor result obtained by removal with a mixture of ethanol and white spirit (1:1). (bottom) A satisfactory result obtained by removal with a mixture of isopropanol, water, and ammonia (9:1:1), where the overpaint was evenly removed and the varnish was preserved.

combinations thereof. In the trials carried out near the inscription, the best results were obtained by means of 3 minute poultice applications combined with a final solvent treatment with a cotton swab. However, in the area of the nimbus, which dates to the same alteration and has the same kind of binder, the best results were obtained using 15 minute poultice applications combined with a final mechanical cleaning with a scalpel. Finally, the established adequate overpaint removal procedures were employed for respective areas of the painting.

CONCLUSIONS

OCT imaging has proved useful in resolving certain problems during conservation of this eighteenth-century painting. It was possible to assess the integrity of the overpainted primary layers and to evaluate the results of overpaint removal in a fast and noninvasive way. This was a valuable aid, especially in the process of revealing the hidden inscription.

Acknowledgments

This work was supported by Polish government research grants for the years 2008–2011. Magdalena Iwanicka additionally acknowledges support from the Foundation for Polish Science within the Ventures Program, cofinanced by Operational Programme Innovative Economy within the European Regional Development Fund.

REFERENCES

Liang, H., B. Peric, M. Spring, D. Saunders, M. Hughes, and A. G. Podoleanu. 2008. "Non-Invasive Imaging of Subsurface Paint Layers with Optical Coherence Tomography." In *Conservation Science 2007*, ed. J. H. Townsend, L. Toniolo, and F. Cappitelli, pp. 171–176. London: Archetype Publications.

Szkulmowska, A., M. Góra, M. Targowska, B. Rouba, D. Stifter, E. Breuer, and P. Targowski. 2007. "The Applicability of Optical Coherence Tomography at 1.55 μm to the Examination of Oil Paintings." In *Lasers in the Conservation of Artworks, LACONA VI Proceedings*, ed. J. Nimmrichter, W. Kautek, and M. Schreiner, pp. 487–492. Berlin: Springer.

Targowski, P., M. Iwanicka, L. Tymińska-Widmer, M. Sylwestrzak, and E. A. Kwiatkowska. 2010. Structural Examination of Easel Paintings with Optical Coherence Tomography. *Accounts of Chemical Research*, 43(6):826–836. http://dx.doi.org/10.1021/ar900195d.

Extended Abstract—A New Documentation System: Stratigraphic Units Recording Sheets Applied to the Cleaning of a Fifteenth-Century Painting

José Manuel Barros García and Eva Pérez Marín

INTRODUCTION

At the beginning of the twenty-first century, a new direction began developing in the stratigraphic study of painted surfaces thanks to the use of stratigraphic diagrams and stratigraphic unit recording sheets. Harris's (1989) work in the field of archaeology brings important inspiration from what would appear to be a completely different field. It is indeed still innovative for painting conservation despite having been introduced in the study of ancient architecture some decades ago for the study of wall plasters.

The title of a paper by Harris (2006), "Archaeology and the Ethics of Scientific Destruction," perfectly highlights the importance of recording everything that will be destroyed. This concept is vital in an archaeological excavation, just as it is in the cleaning of a culturally significant object. The importance given nowadays to the nonoriginal deposits present in an object's surface is relatively recent. Traditionally, the restorer was more worried about recovering the original work, and therefore, the nonoriginal layers were nothing more than a troublesome barrier that hid the object and that had to be destroyed at all costs. Although such deposits must be removed, today, it is considered of key importance to document their existence in the most precise way possible. These deposits do, in fact, constitute a valuable archive that retains important information about how an object was produced, preserved, and displayed, about the chemical and physical changes undergone by original and nonoriginal materials, and even about social context or man's way of thinking during a given period in history.

Each strata or layer (varnish, filler, overpaint, etc.) is called a stratigraphic unit (SU), the smallest meaningful unit of the stratigraphic study, which has its own particular physical characteristics. The strata are the positive units, and the losses, which must also be recorded, are the negative units. A SU should be recorded according to three types of main data: the description of its physical characteristics (e.g., color, texture, composition), its location on the plan, and its relationships with the other units (where the SU is situated within the stratigraphic sequence). All this information is gathered together on a recording or data sheet, which thus becomes the central element of the documentation system.

***José Manuel Barros Garcia** and **Eva Pérez Marín**, Instituto Universitario de Restauración del Patrimonio, Universidad Politécnica de Valencia, Camino de Vera, s/n, 46022 Valencia, Spain. Correspondence: José Manuel Barros Garcia, jobargar@crbc.upv.es.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

The SU data sheet makes the conservator observe more rigorously the different strata and their relationships during the cleaning process and compels the restorer toward a logical approach to complicated stratigraphic situations. With this system of documentation the conservator must necessarily approach the cleaning process from an analytical point of view, attentive to details and cautious in the identification of each SU. This system of documentation requires layer by layer removal, identifying and studying each new SU and its relationships with the other units. This allows a standardized documentation to be obtained that can be studied by any given researcher in order to understand how the nonoriginal layers were arranged before cleaning and exactly how the cleaning was carried out. Basically, the main idea is to think of the cleaning process in terms of an archaeological excavation. This methodology has been used for the documentation of various cleanings, with very good results (Barros García, 2004, 2009).

PRACTICAL APPLICATION

The system can be illustrated with the example of the recording carried out for the cleaning of the panel painting *St. Matthias and St. Philip* by Paolo da San Leocadio (second half of the fifteenth century), which is in a private collection in Madrid (Figure 1). In contrast to the original layers, the materials deposited over time can be removed following a stratigraphic approach during cleaning (Figure 2). This approach provides a great amount of information, which is not always easily accessed by mere observation of the surface or cross-sectional studies. The main nonoriginal layers identified in *St. Matthias and St. Philip* were the following: dirt (SU1), overpaint (SU4, SU5, SU6, SU7, SU8, SU9, SU10, SU12, SU15, SU16, SU17, SU18, SU19, SU20, SU21, SU22, SU24, SU29, SU33), varnish (SU2), fillers (SU13, SU25, SU27, SU28, SU30), and wax (SU31).

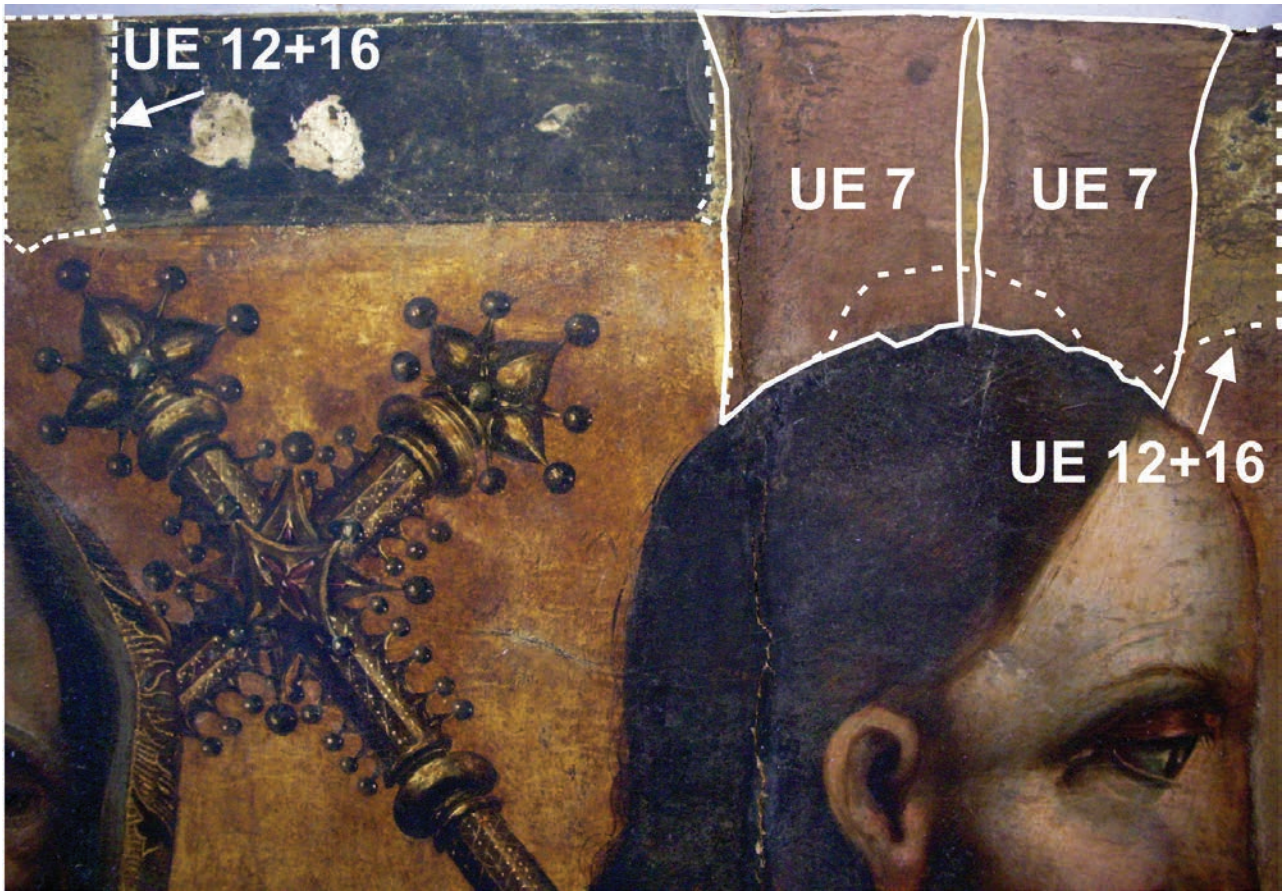


FIGURE 1. The painting during the cleaning process (detail).

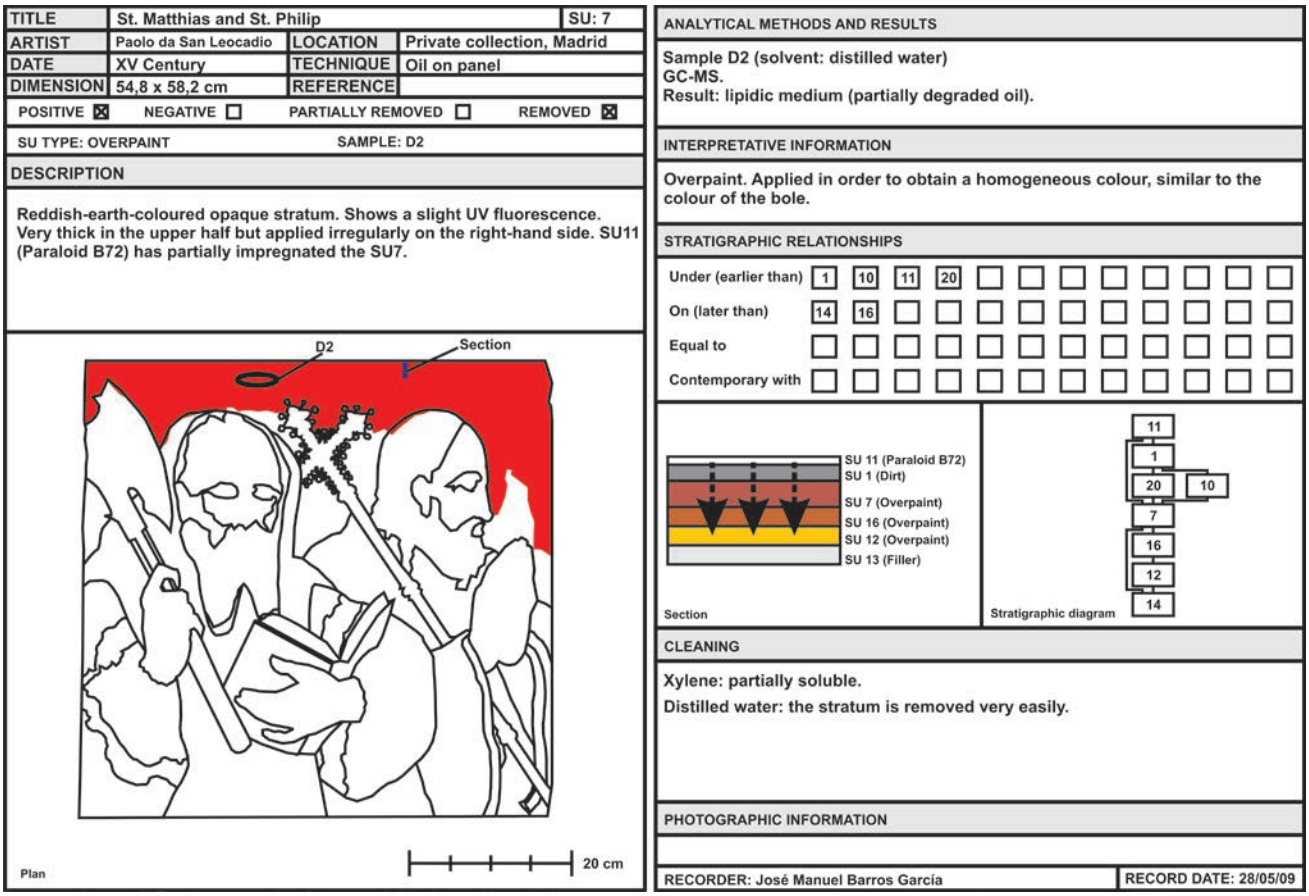


FIGURE 2. Recording sheet of stratigraphic unit 7.

Stratigraphic study and cleaning are two processes that necessarily go together. Thus, the surface becomes a unique field of exploration in order to gain insight into an object's past and thereby also a better understanding of its present.

REFERENCES

Barros García, J. M. 2004. The Use of the Harris Matrix to Document the Layers Removed during the Cleaning of Painted Surfaces. *Studies in Conservation,* 49:245–258. http://dx.doi.org/10.2307/25487701.

———. 2009. Recording Stratigraphic Relationships among Non-original Deposits on a 16th Century Painting. *Journal of Cultural Heritage,* 10:338–346. http://dx.doi.org/10.1016/j.culher.2009.01.001.

Harris, E. C. 1989. *Principles of Archaeological Stratigraphy*. 2nd ed. London: Academic Press.

———. 2006. "Archaeology and the Ethics of Scientific Destruction." In *Between Dirt and Discussion,* ed. S. N. Archer and K. M. Bartoy, pp. 141–150. New York: Springer.

Extended Abstract—Computer Applications and Cleaning: Teas Fractional Solubility Parameter System in Conservation

Amparo Saera Vila and José Manuel Barros García

The solubility triangle is a useful tool to predict the effectiveness of a solvent or a solvent mixture in the elimination of a particular substance. A further advantage of this tool, as increased awareness of health issues for the restorer are becoming apparent, is the use of solubility parameters to substitute toxic solvents with less toxic ones.

This study carried out a comparative evaluation of three software applications that facilitate the use of the solubility triangle. The three computer programs are Triansol, Trisolv, and Solvent Solver. Using these applications, it was easy to find solvent mixtures that would be more effective in addressing a given problem. Moreover, they allow searching for equivalent or substitution solvents in a fast and comfortable way (Figure 1).

The Triansol software was created by Cremonesi and Bortolotti (1999) on the basis of some aspects of Feller's test (Feller, 1976). It can search solvents or solvent mixtures with certain solubility parameters fast and efficiently. It has a database of 27 solvents, but others can be added as required. In turn, the results are stored in another database. Of the three programs mentioned in this article, it is the only one that is not available free of charge through the Internet.

Trisolv (Figure 2) is an online working tool, created by Mauricio Coladonato and Paolo Scarpitti, and it can be accessed through the Web site of the Istituto Superiore per la Conservazione ed il Restauro (Coladonato and Scarpitti, n.d.). Its advantages include a display of different areas of solubility and the possibility of working in several languages.

The third program is Solvent Solver (Figure 3), created by Mark Ormsby (2006) in order to calculate mixtures of two or three solvents with particular solubility parameters. It also has the option of calculating the parameters of a mixture. Its biggest advantage is the accuracy of the mixing parameters and the stringency on the toxicity issue.

It cannot be denied that the solubility triangle offers only an approximation to the problem of predicting the behavior of solvent mixtures. There are 3-D models that are more accurate (Burke, 1984), but they are also far more difficult to use. Some critics are very harsh concerning the usefulness of the triangle (Stavroudis and Blank, 1989); although taking into account its obvious limitations, e.g., the results are not always very accurate, it can be of some use when designing solvent mixtures.

Each of the three programs has advantages and disadvantages. The best answer has been found by working with the three programs in combination. This results in an excellent approach to selecting the best solvent, or combination of them, for the particular problem to be addressed. Nonetheless, it can be said that the Triansol software is the most complete tool because it offers the possibility of obtaining reliable results in a quick

***Amparo Saera Vila**, Avenida Mediterraneo 15, 12530 Burriana, Castellón, Spain. **José Manuel Barros García**, Instituto Universitario de Restauración del Patrimonio, Universidad Politécnica de Valencia, Camino de Vera, s/n, 46022 Valencia, Spain. Correspondence: Amparo Saera Vila, amparosaera@hotmail.com; José Manuel Barros García, jobargar@crbc.upv.es.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

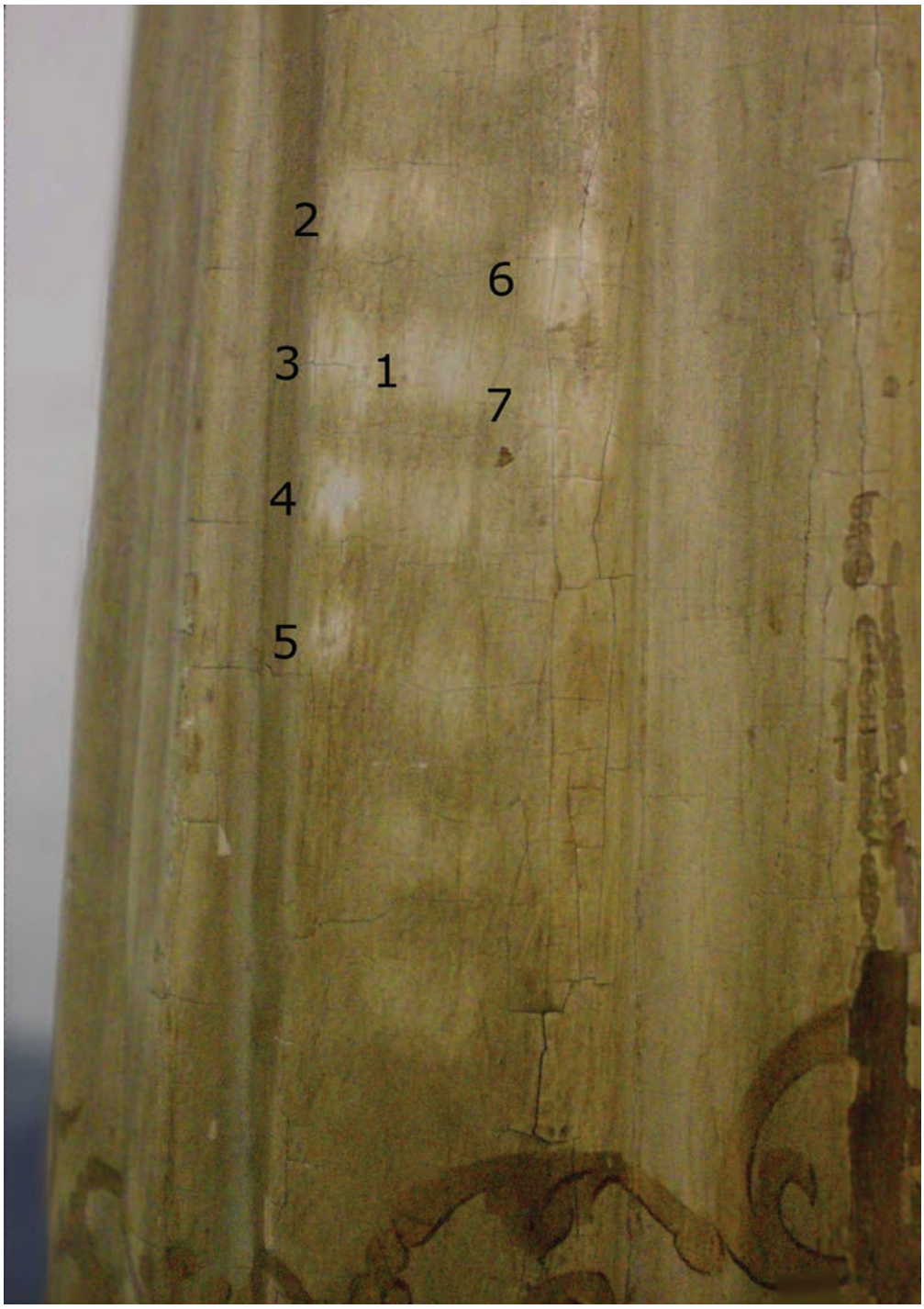


FIGURE 1. Different cleaning mixtures were tested on a polychrome sculpture, labeled 1 to 7 on the photograph. All mixtures had the same solubility parameters, i.e., f_d = 64, f_p = 19, and f_h = 17. The mixtures were as follows: 1, 50% acetone, 50% toluene; 2, 57% turpentine, 43% acetone; 3, 40% turpentine, 39% *n*-butylacetate, 21% acetone; 4, 51% acetone, 36% isooctane, 13% ethanol; 5, 53% 2-butanone, 29% nonane, 18% isopropyl alcohol; 6, 37% *n*-butyl acetate, 32% diethyl ketone, 31% turpentine; 7, 58% diethyl ketone, 42% dipentene. It can be seen that different mixtures with the same solubility parameter will not always be equally effective.

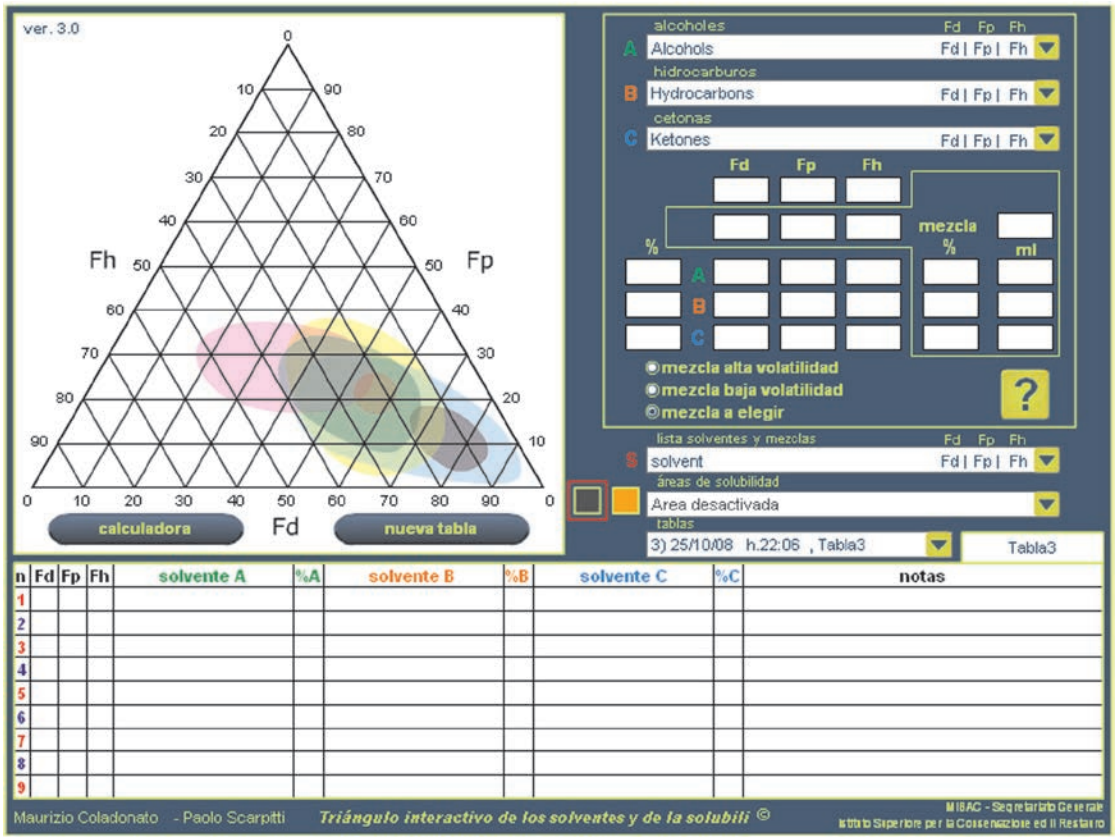


FIGURE 2. Trisolv software main window.

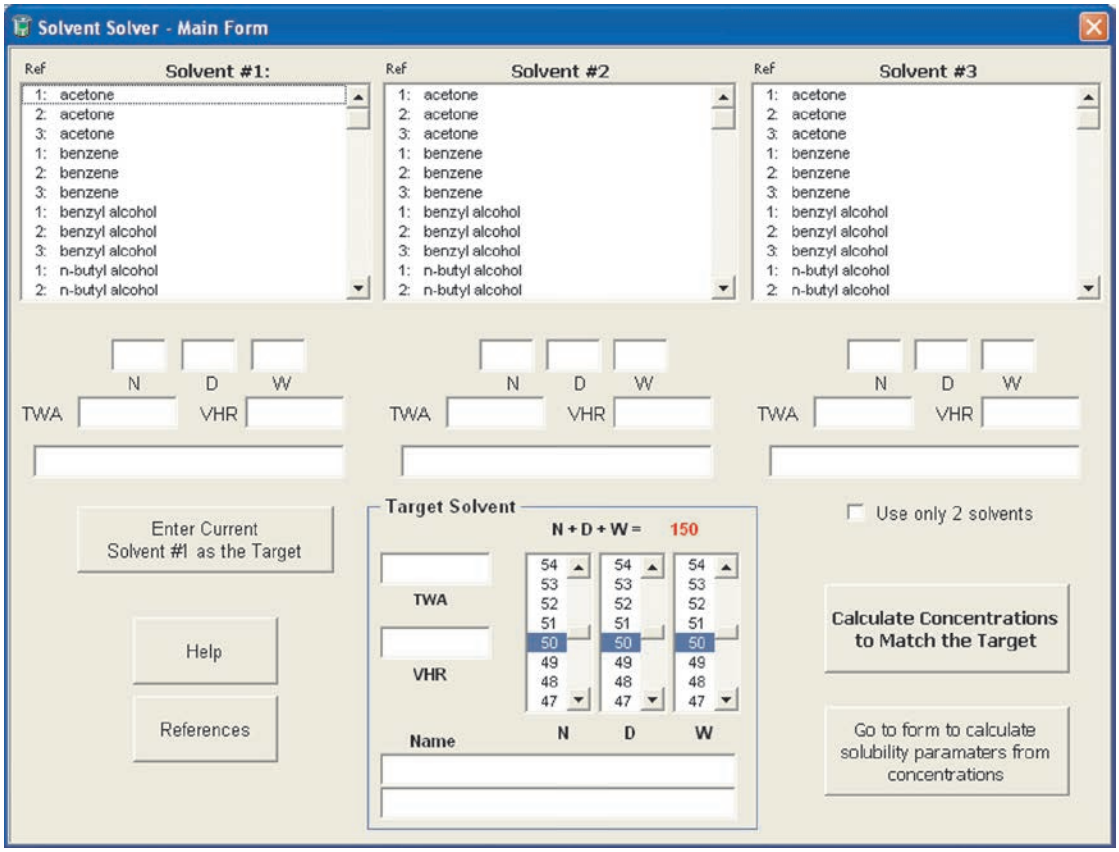


FIGURE 3. Solvent Solver software main window.

and easy way as well as the ability to store them in a database. This decision is also supported by the fact that new solvents can be added to the database and that, having the largest number of solvents, it offers far more variability in the mixtures that can be created.

REFERENCES

Burke, J. 1984. "Solubility Parameters: Theory and Application." In *AIC Book and Paper Group Annual*, Volume 3, ed. C. Jensen, pp. 13–58. Washington, D.C.: American Institute for Conservation. http://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html (accessed 15 February 2012).

Coladonato, M., and P. Scarpitti. n.d. References of the Interactive Solvent and Solubility Triangle©. http://iscr.beniculturali.it/flash/progetti/TriSolv/TriSolv.html (accessed 15 February 2012).

Cremonesi, P., and I. Bortolotti. 1999. Un approccio più scientifico alla pulitura dei dipinti. Triansol®: Il triangolo delle solubilità, un software per il restauro. [A More Scientific Approach to the Cleaning of Paintings. Tiransol®: The Solubility Triangle, a Software for Restorers.] *Progetto Restauro,* 10:42–45.

Feller, R. L. 1976. "The Relative Solvent Power Needed to Remove Various Aged Solvent-Type Coatings." In *Conservation and Restoration of Pictorial Art*, pp. 158–161. London: Butterworths.

Ormsby, M. 2006. Solvent Solver: A Calculator for Working with Teas Fractional Solubility Parameters. http://cool.conservation-us.org/packages/solvent-solver/solvent_solver.html (accessed 15 February 2012).

Stavroudis, C., and S. Blank. 1989. Solvents & Sensibility. *WAAC Newsletter,* 11(2):2–10. http://cool.conservation-us.org/waac/wn/wn11/wn11-2/wn11-202.html (accessed 15 February 2012).

The Chemistry of Egg Binding Medium and Its Interactions with Organic Solvents and Water

Antonella Casoli, Michela Berzioli, and Paolo Cremonesi

ABSTRACT. The aim of this study was to gain a deeper insight into the properties of egg, used as a binding medium, and its interactions with water and organic solvents. The research focused on egg tempera films prepared in July 2007 and on a tempera layer prepared by researchers of the Smithsonian's Museum Conservation Institute in 1995. It also included a sixteenth-century panel painting from the Pinacoteca di Siena. Two paint samples from this painting were analyzed by gas chromatography coupled with mass spectrometry and identified egg as the binding medium. Ethanol or acetone, isooctane, and water were used to test for leaching. In general, the main leaching occurs from the fresher samples: using solvents of different polarity (from isooctane to water), the lipid components are the most removed. It also was observed that pigmented layers are less affected by leaching phenomena than a layer without pigments, in particular for lipid components. Finally, it was noticed that unsaturated fatty acids were extracted mainly from fresh samples, with less from the 1995 tempera and nothing from the sixteenth-century painting. However, the study carried out on this painting showed that leaching is more pronounced for the lipid components, and amino acids were also detected. These results were unexpected because mild cleaning tests were believed not to affect a 500-year-old painting. These results might be regarded as guidelines to take into account for cleaning paintings.

INTRODUCTION

Egg tempera techniques employ the whole egg, or egg yolk and egg white separately, for binding media purposes, in which pigments are dispersed, sometimes combined with other materials, i.e., fig latex and cherry gum, depending on the painter's requirements. Egg tempera was traditionally used in the past, especially in the fourteenth and fifteenth centuries in Italian painting.

Because detailed studies are available on this topic (Thompson, 1936; Boon et al., 1997; Phenix, 1997), only a general description will be provided. Egg binding medium is made up of proteins, lipids, polysaccharides, and inorganic compounds. Egg white is a diluted water solution of proteins (mainly ovalbumin) and a small fraction of polysaccharides. Once applied, this material becomes insoluble.

Egg yolk contains mostly lipids (66% in terms of mass) and proteins, as well as small amounts of polysaccharides and inorganic compounds. Lipids are present in the yolk as triglycerides (neutral lipids), phospholipids, and cholesterol. Triglycerides, the main lipids, are the same type of compound as drying oils. However, in egg these lipids contain less unsaturated fatty acids compared to oils. The fatty acid distribution in yolk lipids is saturated 38%, monounsaturated 42%, and polyunsaturated 20%. Their drying properties are not as strong as oils, but they are subject to the same oxidative polymerization reactions that

Antonella Casoli *and* ***Michela Berzioli****, Dipartimento di Chimica, Università degli Studi di Parma, viale G.P. Usberti, 17/a, 43124 Parma, Italy.* ***Paolo Cremonesi****, Cesmar7–The Centre for the Study of Materials for Restoration, Via Lombardia 41/43, 35020 Saonara, Italy. Correspondence: Antonella Casoli, antonella.casoli@unipr.it; Michela Berzioli, michela.berzioli@libero.it; Paolo Cremonesi, paolocremonesi57@gmail.com.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

occur in linseed oil. One main difference is that egg yolk contains polymeric material (proteins). For this reason egg is considered a proteinaceous material, although this is not correct. In fact, this binding medium becomes extremely resistant when applied and aged because of the polymerization of its lipid component.

The lipids contained in egg yolk have the same characteristics as small molecules in a drying oil. A plasticizer action can then be hypothesized, and consequently, structural damage can result if the lipids are removed by using solvents during cleaning. The main preliminary work (Khandekar et al., 1994) seems to support this hypothesis. Complexity increases as the medium starts aging and undergoes chemical changes as a result of oxidation processes and interactions among the different components, with lipid oxidation and related radical reactions, cross-linking, and chain scission being the main reactions.

Shortly after the application of egg tempera, lipids can be extracted with several solvents: alcohols, ketones, and aromatic and chlorinated hydrocarbons. Consequently, the film undergoes contraction and shows superficial alterations. In artificial aging tests, some of these lipids have proved to be very mobile and tend to come to the surface spontaneously, and the most volatile ones tend to evaporate. As for the case of drying oils, the material may form a superficial patina at the interface with the eventual varnish, if present.

The lipid amount removable with solvents decreases considerably with aging. The mechanisms responsible for the film hardening during aging are fairly well known (Karpowicz, 1981; Boon et al., 1997; Phenix, 1997).

The resistance to different-polarity organic solvents and to water was checked on egg tempera samples made up of several pigments (white lead, vermilion, verdigris, azurite) and artificially aged (Khandekar et al., 1994). It was noted that hydrocarbons, such as dichloromethane, and acetone cause leaching of the lipid components on a recently formed film, whereas water causes film swelling. The extraction of these components causes film damage.

In past studies (White and Roy, 1998), the interaction of organic solvents with paint layers during cleaning operations (removal of a resinous varnish) of real paintings, including an egg tempera one, as well as that of unaged samples was explored. It was noted that the two solvents tested (2-propanone and 2-propanol [isopropyl alcohol]) did not appear to cause any leaching of the oil paints either from the unaged samples or the real paintings, not even in the case of the egg tempera painting.

Therefore, the aim of the present study was to gain a deeper insight into the properties of the egg binding medium, which was very important in Italian artistic tradition for several centuries, and its interactions with water and organic solvents. This research focused on studying (1) recent egg tempera films, prepared in our laboratory following the recipes in Cennino Cennini's treatise (Cennini, 1437) in July 2007 (Berzioli et al., 2009), (2) a tempera layer prepared by researchers at the Smithsonian's Museum Conservation Institute in 1995, and (3) a sixteenth-century painting from the Pinacoteca Nazionale in Siena. Two paint samples from this painting were analyzed by gas chromatography coupled with mass spectrometry (GC-MS), which identified egg as the binding medium.

The leaching of soluble components, caused by solvent application to the egg layers, was studied. Isooctane, acetone or ethanol, and water were applied by means of cotton swabs, lightly rolled over the egg tempera layers. The components extracted were identified by means of GC-MS. The color changes of the layers, before and after treatment with solvents, were studied by means of a multispectral scanner.

EXPERIMENTAL METHODS

Preparation of the Tempera Layers on Wood Panels

Following Cennino Cennini's description in his treatise (Cennini, 1437), a priming layer of four coats of animal glue and gypsum was applied onto several wooden panels. A binding medium made of egg yolk, cherry gum, and fig latex in a 10:10:1 ratio by volume (T) was then applied to rectangular sections of one panel. On another panel, layers of pigmented binding media of the same composition were prepared, one with vermilion (T-V) and one with minium (T-M). Two grams of each pigment were mixed with 2 mL of binding medium. The same layers (T, T-V, and T-M) were also applied onto glass slides for microscope observation. Once prepared, the panels were left to dry for about four months prior to the first solvent treatment.

Application of Organic Solvents and Distilled Water onto the Egg Tempera Layers

Ethanol or acetone, isooctane, and water were applied to the egg tempera layers by lightly rolling cotton swabs (previously rinsed in hexane, ethanol, and water and vacuum dried). Three drops of solvent were added to each swab and then rolled on the tempera for 15 s or 30 s on a 1 × 2 cm area. Afterward, the cotton swabs were transferred into vials and stored at 4°C.

Stereomicroscopic Investigation and Colorimetric analysis

The layers were observed under a stereomicroscope in order to monitor their morphology. The spectral reflectance factors were measured on fixed areas, and CIE L*a*b* values were calculated to obtain color specification of the surfaces. Lighting and observation conditions were 45/0° with a halogen lamp, and a D65 illuminating agent and CIE 1931 observer were considered. The spectrophotometric scanner (spectral region: 380–800 nm) used was developed by researchers of University of Parma (Antonioli et al., 2004).

GC-MS Analyses of Lipids, Proteins, and Cholesterol Fractions Extracted from Tempera Layers

For each tempera layer, cotton swabs (with solvents, i.e., ethanol, isooctane, and water, and without any solvent, i.e., dry swabbing, performed in triplicate tests) were analyzed for fatty acids, amino acids, and cholesterol. All procedures for analysis were repeated at least twice.

The chromatographic peak area of each analyte was integrated, corrected by a response factor, and expressed in relation to the internal standard (IS) in order to obtain quantitative information. Finally, the average analyte/IS ratio was calculated, and the average percentage of three runs was determined.

For cholesterol analysis, the cotton swabs used for cleaning were placed in a test tube for hexane extraction (1 mL of IS, 10 parts per million (ppm) stigmasterol in hexane, was added). Through a derivatization procedure the cholesterol was turned into trimethylsilylated cholesterol (Annaratone et al., 2009).

For analyses of lipids and proteins the cotton swabs were extracted for 30 minutes with 2 mL of the same solvent used for cleaning, under magnetic stirring in warm conditions (about 50°C). Then the cotton was removed and the solvent was evaporated under vacuum conditions. The following internal standards were added to the residue: 10 µL of a 1000 ppm heptadecanoic acid in hexane solution and 10 µL of a 1000 ppm norleucine in water solution. Thus, the samples were derivatized (Casoli et al., 2001). A gas chromatograph 6890N GC (Agilent Technologies) coupled to a Mass Selective detector (5973, Agilent Technologies) was used.

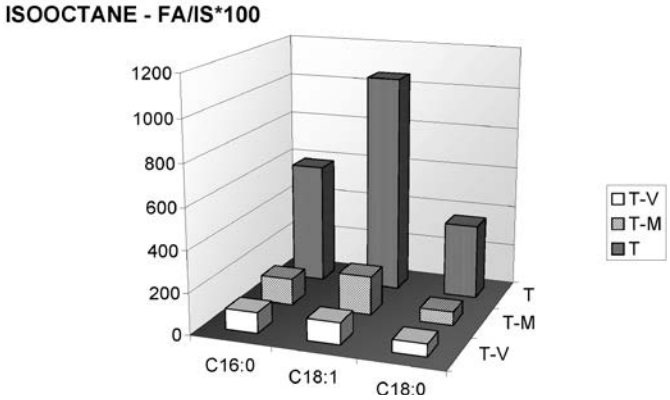


FIGURE 1. Histogram of fatty acids extracted by isooctane on the pigmented (T-V and T-M) and the unpigmented (T) tempera films. Each value represents the average percentage ratio of analyte to internal standard (IS). C16:0 is palmitic acid, C18:1 is oleic acid, and C18:0 is stearic acid.

RESULTS AND DISCUSSION

Laboratory Tempera Samples

Ethanol, isooctane, and water were applied to the egg tempera layers by lightly rolling cotton swabs. Three drops of solvent were added to each swab and then applied to the tempera for 30 s on an area of 2 cm^2. Observation of the laboratory samples' surfaces (T, T-V, T-M) by means of stereomicroscope before and after the treatment with ethanol, isooctane, and water did not show significant differences. No mechanical abrasion of the surfaces of the egg tempera films was noticed.

The spectral reflectance factor and the coordinate values (CIE L*a*b*) were measured before and after the treatments. It was observed that for the binding medium layer (T), organic solvent treatments caused a very slight increase of the spectral reflectance factor, probably because of an insignificant thinning of the layer. Instead, the application of water to the T layer showed a very slight decrease of the spectral reflectance factor. One explanation could be that the surface may have darkened because of dust collecting over time. It was interesting to notice that the two pigmented layers showed the same behavior after ethanol, isooctane, and water treatments. It was noted that in the 600–700 nm interval the spectral reflectance factor decreased after treatment: this might be due to a slight darkening of the layer caused by solvent action. Nevertheless, all these measured effects were not visually perceptible.

All the cotton swabs, applied to the layers with each of the three solvents and without solvents, i.e., by dry swabbing, were analyzed by means of GC-MS. The chromatographic analyses showed the presence of fatty acids, amino acids, and cholesterol in all the cotton swabs analyzed. It was observed that the mechanical action was able to remove material. It was noticed that only isooctane applications caused a higher degree of extraction compared to that without solvents.

Regarding fatty acid analysis, palmitic acid (C16:0), stearic acid (C18:0), and unsaturated oleic acid (C18:1) were identified. Figure 1 shows the trend of fatty acids extracted by isooctane applied on all the layers. The amount of oleic acid extracted from the T layer was about 100 µg, calculated by means of the internal standard.

The behavior of the three solvents related to cholesterol was then considered. The swabs without solvent extracted cholesterol at a trace level, in similar amounts to the application of water and ethanol. Isooctane was the solvent that removed the most cholesterol (Figure 2); some 50 µg of this compound were

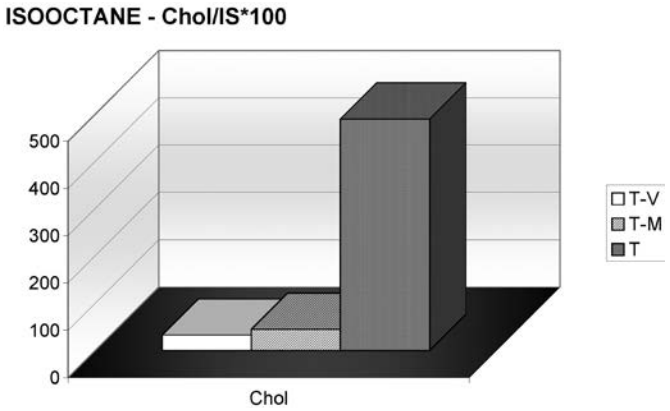


FIGURE 2. Histogram of cholesterol extracted by isooctane on the pigmented (T-V and T-M) and the unpigmented (T) tempera films. Each value represents the average percentage ratio of analyte to internal standard (IS).

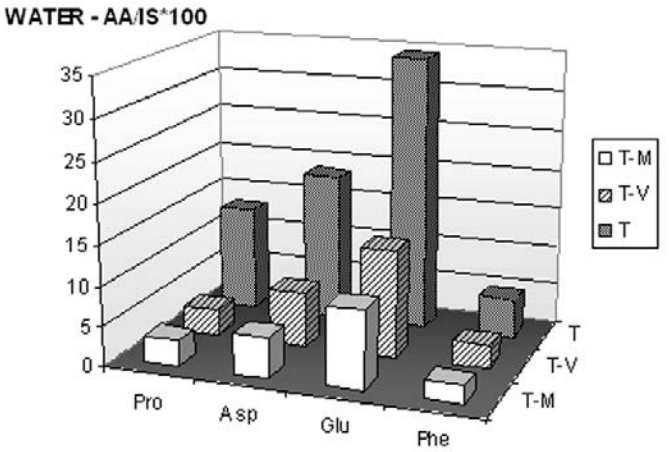


FIGURE 3. Histogram of some amino acids extracted by water from the tempera films. Each value represents the average percentage analyte to internal standard (IS) ratio. Pro = proline, Asp = aspartic acid, Glu = glutamic acid, and Phe = phenylalanine.

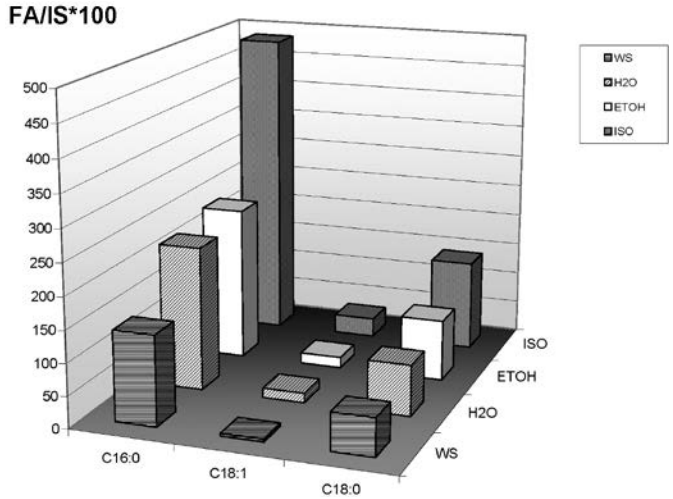


FIGURE 4. Histogram of fatty acids extracted by water (H_2O), ethanol (EtOH), and isooctane (ISO) and without solvents (WS) on the egg tempera layer from 1995. Each value represents the average percentage analyte to internal standard (IS) ratio.

detected in the swabs from the binding medium alone, whereas a small amount was observed in the pigmented layers (ratio of about 10:1).

The chromatographic results showed that the amino acids from proteinaceous material were only extracted by swabs with water. The histogram in Figure 3 shows the results of the proteinaceous fraction for the water application on layers, taking into account four amino acids: proline, aspartic acid, glutamic acid, and phenylalanine. The proteinaceous fraction extracted was very low in comparison to lipids (ratio of about 1:30).

The Smithsonian's Museum Conservation Institute Sample

A sample composed of egg tempera layered onto a Melinex polyester film, prepared in 1995, was also analyzed. The first GC-MS analyses carried out confirmed the presence of egg as a binding medium. Water, ethanol, and isooctane were applied by means of cotton swabs lightly rolled over the egg tempera layer for 15 s on an area of 1 cm^2.

Using the stereomicroscope, it was observed that the surface originally appeared greasy, but after solvent treatments, it lost this glossy appearance. The colorimetric analyses measured small variations due to solvent treatments, except for the case of ethanol applications where color changed in a visually perceptible way; the measured change was $\Delta E = 3.23$.

The GC-MS fatty acids analyses carried out on the cotton swabs (with and without solvents) showed palmitic acid (C16:0), oleic acid (C18:1), and stearic acid (C18:0). The histogram in Figure 4 shows that isooctane is the best leaching agent, removing 25 ng of palmitic acid.

It is interesting to note that more saturated fatty acids were removed than oleic acid, in spite of the fact that oleic acid is more abundant than stearic acid in egg tempera. The saturated fatty acids were probably present on the surface because of a migration effect because the support of the film was not transpiring. This would also explain the original greasy surface.

A small amount of cholesterol was detected only in the cotton swabs with isooctane. From the proteinaceous fraction, the amino acids peaks are comparable to the analytical blank for all cotton swabs.

Case Study: A Painting from the Sixteenth Century

Cleaning tests were carried out on the painting *Caduta di Gesù sotto la croce, fra i Santi Pietro, Michele Arcangelo, Angelo col piccolo Tobia, e Paolo* (Jesus at the Foot of the Cross, between Saint Peter, the Archangel Michael, and an Angel with the Small Tobia, and Saint Paul) by an unknown artist from around the middle of the sixteenth century (Figure 5). It is a small painting on wood (21.5 × 79.5 cm^2), probably part of an altar step, conserved in Pinacoteca Nazionale in Siena. The painted parts were all on gold: the board was gilded and then painted. This artwork appeared ideal for our purposes because it was done with egg tempera and it had not been varnished or restored.

The cleaning tests were carried out with three solvents with different polarities (water, acetone, and isooctane) in the same working conditions and on adjacent areas of the artwork in order to verify whether any leaching occurred because of the treatments. It was observed that isooctane was able to extract

FIGURE 5. Detail of the sixteenth-century painting *Caduta di Gesù sotto la croce, fra i Santi Pietro, Michele Arcangelo, Angelo col piccolo Tobia, e Paolo*, indicating one of the sampled areas.

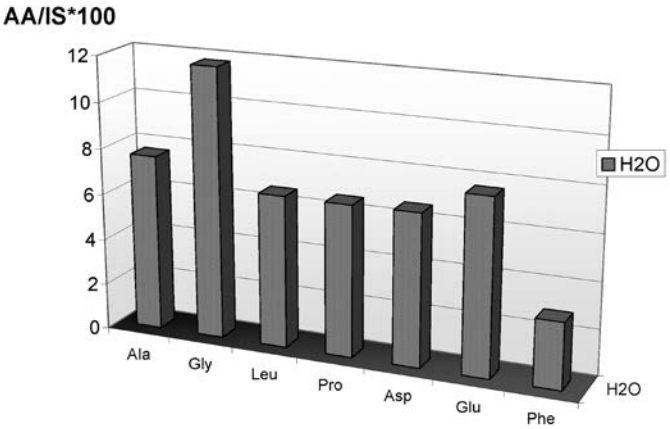


FIGURE 7. Histogram of amino acids extracted by water on the painting's surface. Each value represents the average percentage analyte to internal standard (IS) ratio.

both palmitic and stearic acids. With regard to cholesterol, in all the cotton swabs, its peak was comparable to an analytical blank. However, amino acids were detected in the water swabs. Figures 6 and 7 show the corresponding histograms. It can be seen that more fatty acids were extracted than amino acids.

From the results it can be inferred that isooctane, the most nonpolar solvent tested, removed the lipid fraction, whereas water partially removed the proteinaceous fraction. Acetone was observed to extract less fatty acid than the isooctane. As expected, unsaturated fatty acids were not detected; in fact, in this 500-year-old painting the polymerization process is complete.

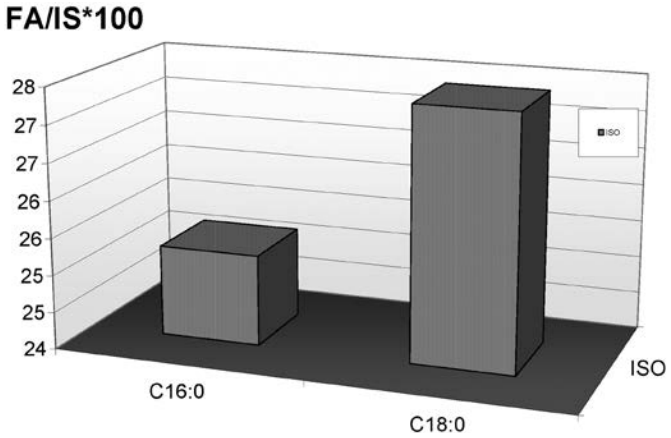


FIGURE 6. Histogram of fatty acids extracted by isooctane on the painting's surface. Each value represents the average percentage ratio of analyte to internal standard (IS).

However, the fact that both fatty acids and amino acids were extracted, even if the amounts extracted were about 50 times lower than those for the laboratory samples, was completely unexpected for a sixteenth-century painting.

CONCLUSIONS

Color changes, as a result of the interaction of organic solvents and water on egg binding medium carried out on laboratory samples, proved to be visually imperceptible, although changes were instrumentally measurable. Analyses of the cotton swabs applied without solvents showed the presence of fatty acids, amino acids, and cholesterol and confirmed that mechanical action alone was able to remove material. When solvents were used on the cotton swabs, the results depended on their polarity: isooctane removed mainly fatty acids and cholesterol, and water removed only amino acids. It was observed that the leaching ability of isooctane is 30 times greater than that of water.

It was confirmed that pigmented layers are less affected by leaching phenomena than pigment-free layers, particularly for lipid components. This finding may be linked to two factors: (1) The first is a physical-morphological factor; when the pigment is dispersed in it, the binding medium is obviously reduced. (2) The cations could bind to fatty acids, forming metal soaps and making the fatty acids less sensitive to leaching.

The analysis from all cotton swabs, with and without solvents, obtained from the egg tempera prepared at the Smithsonian's Museum Conservation Institute shows the presence of these fatty acids in decreasing order: palmitic acid (C16:0), stearic acid (C18:0), and oleic acid (C18:1). Cholesterol was removed in very small amounts relative to fatty acids. Apparently, no proteinaceous material was extracted. It was observed that the lipid

fraction is only present on the surface, rendering it hydrophobic; this was attributed to a migration effect because of the nonpermeable support. Interestingly, more saturated fatty acids were removed than oleic acid, in spite of the fact that oleic acid is more abundant than stearic acid in egg tempera. This is not surprising considering that unsaturated fatty acids become less mobile when they take part in the polymerization process.

The study on the sixteenth-century panel painting showed that the leaching phenomenon was greater for lipid components but that amino acids were also extracted. As expected, unsaturated fatty acids were not detected; in fact, in a 500-year-old painting the polymerization process is complete. The extraction content results were about 50 times lower compared to the laboratory samples. These results are unexpected because mild cleaning tests were believed to be safe and undamaging for a 500-year-old painting. These results might be regarded as guidelines for cleaning paintings.

Further research with other organic solvents and water solutions at different pHs is being carried out on laboratory panels and will also be tested on ancient tempera paintings.

Acknowledgments

The authors are grateful to Giovanni Antonioli, Cinzia Bignamini, Elisa Campani, Sara Capretti, Clelia Isca, Remo Reverberi, and Laura Spina of the University of Parma for their contribution to this research, as well as to Anna Maria Guiducci of the Pinacoteca Nazionale in Siena. The authors gratefully thank Marion Mecklenburg of Smithsonian Museum Conservation Institute for providing the aged tempera samples.

REFERENCES

Annaratone, C., A. Caligiani, M. Cirlini, L. Toffanin, and G. Palla. 2009. Sterols, Sterol Oxides and CLA in Typical Meat Products from Pigs Fed with Different Diets. *Czech Journal of Food Sciences*, 27:219–222.

Antonioli, G., F. Fermi, C. Oleari, and R. Reverberi. 2004. "Spectrophotometric Scanner for Imaging of Paintings and Other Works of Art." In *CGIV 2004, Second European Conference on Colour in Graphics, Imaging, and Vision,* pp. 219–224, Aachen, Germany: Technology Center AGIT.

Berzioli, M., C. Bignamini, E. Campani, A. Casoli, P. Cremonesi, and C. Isca. 2009. "The Study of Egg Tempera Binding Medium and Its Interaction with Organic Solvents: Characterisation of the Preliminary Stage." In *Chemistry and Conservation: Proceedings of the 2nd Residential Summer School in Palermo*, ed. E. A. Varella and E. Caponetti, pp. 17–26. Rome: Centro Stampa De Vittoria Srl.

Boon, J. J., S. L. Peulvé, O. F. van den Brink, M. C. Duursma, and D. Rainford. 1997. "Molecular Aspects of Mobile and Stationary Phases in Ageing Tempera and Oil Paint Films." In *Early Italian Paintings: Techniques and Analysis*, ed. T. Bakkenist, R Hoppenbrouwers, and H. Dubois, pp. 35–56. Maastricht, Netherlands: Limburg Conservation Institute.

Casoli, A., P. Cremonesi, G. Palla, and M. Vizzari. 2001. Application of Gas Chromatography-Mass Spectrometry Analysis to the Study of Works of Art: Paint Media Identification in Polychrome Multi-material Sculptures. *Annali di Chimica,* 91:727–739.

Cennini, C. 1437. *Il Libro dell'Arte*. [The Craftsman's Handbook] Reprint edited by F. Brunello, Vicenza, Italy: Neri Pozza editore, 1982.

Karpowicz, A. 1981. Ageing and Deterioration of Proteinaceous Media. *Studies in Conservation*, 26:153–160. http://dx.doi.org/10.2307/1505885.

Khandekar, N., A. Phenix, and J. Sharp. 1994. Pilot Study into the Effects of Solvents on Artificially Aged Egg Tempera Films. *The Conservator*, 18:62–72. http://dx.doi.org/10.1080/01410096.1994.9995086.

Phenix, A., 1997. "The Composition and Chemistry of Eggs and Egg Tempera." In *Early Italian Paintings: Techniques and Analysis*, ed. T. Bakkenist, R. Hoppenbrouwers, and H. Dubois, pp. 11–20. Maastricht, Netherlands: Limburg Conservation Institute.

Thompson, D. V., Jr. 1936. *The Practice of Tempera Painting*. New York: Dover Publications.

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.

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

***Ken Sutherland**, Conservation Department, Philadelphia Museum of Art, Box 7646, Philadelphia, Pennsylvania 19101-7646, USA. Correspondence: ksutherland@philamuseum.org.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

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 preexisting 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. Tumosa, 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 Ammoniumcitraten. *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.

Oil Paints: The Chemistry of Drying Oils and the Potential for Solvent Disruption

Charles S. Tumosa and Marion F. Mecklenburg

ABSTRACT. Oil paints have been used for hundreds of years in the European tradition of panel and canvas painting. Scores of different formulas have been used to find the correct paint with the desired properties. The alteration of the simple oil and pigment formula has led to elaborate systems with complex aging and solvent behavior. In the early stages of paint aging, the processes of autoxidation and hydrolysis dominate and determine overall structure, whereas hydrolysis determines long-term structural behavior. The ions and small molecules set loose by these processes further complicate the solvent behavior. Early hydrolysis of oils can lead to free fatty acids that can alter the initial chemistry and mechanical properties of paint films. The diffusion of small molecular weight compounds through the films of a painting may be quite extensive, with metal ions influencing drying rates and fatty acid anions (or neutral compounds) affecting stiffness or flexibility as well as forming accretions. Removal of these small compounds by solvents can result in loss of color saturation, as well as in embrittling the paint film by promoting cracking, thus affecting its overall strength and leading to an eventual collapse of the paint structure.

INTRODUCTION

Oil paints have been used for hundreds of years in the European tradition of panel and canvas painting. Scores of different formulas have been used to find a paint with the desired properties. For example, it should dry quickly, but not too quickly; it should be flexible, but not too flexible; and it should not yellow. Attempts to maximize desirable properties in paints have led to considerable alteration from the basic formula of a simple oil and pigment mixture. Each alteration may have both an immediate consequence in the early behavior of the paint and a long-term one that may produce undesirable results.

Oils are esters of carboxylic acids, and for paints, drying oils are used, i.e., unsaturated acids with one, two, or three double bonds, e.g., oleic, linoleic, and linolenic acids. These acids are bound to a trihydroxy alcohol, glycerin, to form the corresponding esters. Two saturated fatty acids, palmitic and stearic acids, are also usually present in smaller amounts (Mills and White, 1987:26–40). Originally, the ability of paints to form dry films depended upon a formulation that, in general, had a larger amount of linolenic acid and, to some extent, linoleic acid. The unsaturated bonds, via an oxidation process, cross-link to form a tangled three-dimensional network. On the other hand, the ester bonds are important to the overall structural integrity of the dried oil film. However, these bonds may be easily hydrolyzed during and after the polymerization reaction, releasing free fatty acids. If hydrolysis of the ester bonds occurs before the film forms, the system becomes more acidic and may react with some of the pigments present in it. This paper analyzes

***Charles S. Tumosa**, Department of Criminology, Criminal Justice and Forensic Studies, University of Baltimore, 1420 North Charles Street, Baltimore, Maryland 21201, USA. **Marion F. Mecklenburg**, Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Road, Suitland, Maryland 20746, USA. Correspondence: Charles S. Tumosa, ctumosa@ubalt.edu; Marion F. Mecklenburg, mecklenburgm@si.edu.*
Manuscript received 19 November 2010; accepted 24 August 2012.

in detail the possible effect of these reactions plus the influence of the presence of metal ions or the addition of solvents on the stability of the formulation over time.

AUTOXIDATION PROCESS

Early scientific work examined oils by measuring weight changes in oil films as the oil dried. The drying of oils and oil paints is an autoxidation process where oxygen from the air is taken up and through a free radical process creates a three-dimensional network of bonds. Some of the oxidation products are small molecules that over time diffuse out of the oil film. Weight changes reflect the net change in weight produced by the uptake of oxygen and the loss of volatiles from the film. Net changes in weight can be considerable, up to a 14% increase or so in the first stages.

After an initial increase of weight due to oxygen take-up, the weight decreases. This reflects the loss of low molecular weight compounds that are diffusing out of the film. These have as yet not been identified. In oils with a lower content of linolenic acid than that of linseed oil, the weight loss may be greater than the early original uptake of oxygen. The weight loss may produce voids or channels within the film affecting its behavior with solvents or even a collapse of the polymer structure. This weight loss from oil paint films predicts that over time the linseed oil–based paints will be less affected by diffusion of solvents than the poppy oil– or walnut oil–based paints because of a smaller loss of weight. Figure 1 plots the long-term weight loss in several oils over 1200 days. Note that the cold-pressed linseed oil loses far less weight than the other ones. Some of the oils are lighter in weight than when first applied, indicating severe degradation of the oil film polymer, which can continue for several years.

Figure 2 shows the weight changes in two red iron oxide paints prepared from cold-pressed linseed oil and a commercial (Kremer Pigments) linseed oil with lead, as litharge (PbO), added as a drier. There is still a measurable weight loss after 10 years, and although the loss remains small, it gives no indication of having stopped. This indicates that there is a loss of fatty acids or similar volatile compounds.

Figure 3 shows the weight changes in two alizarin-based oil paints, one in cold-pressed linseed oil and the other in linseed oil with litharge added as a drier. The long-term behavior is similar to the red iron oxide pigmented paints, i.e., the weight loss

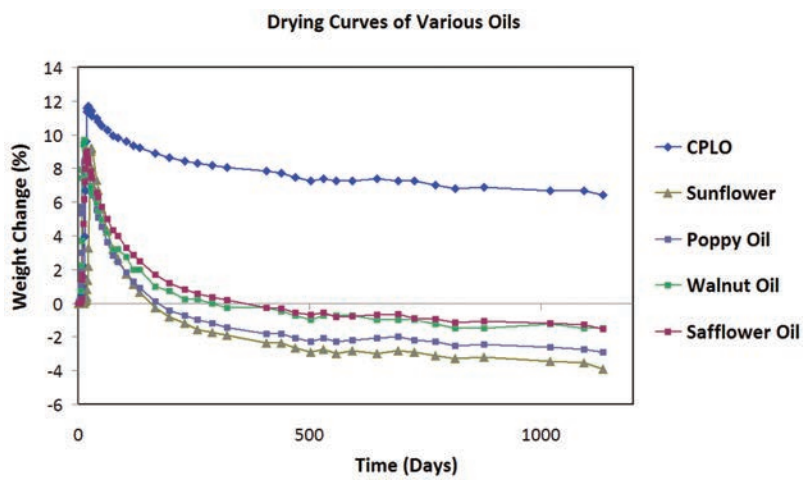


FIGURE 1. The weight changes of pure oils after almost 1200 days of drying. CPLO = cold-pressed linseed oil.

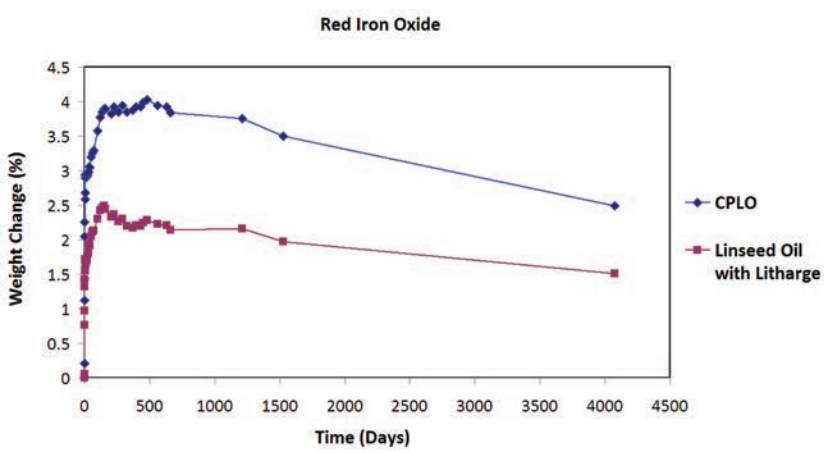


FIGURE 2. Weight changes for two red iron oxide paints over 10 years.

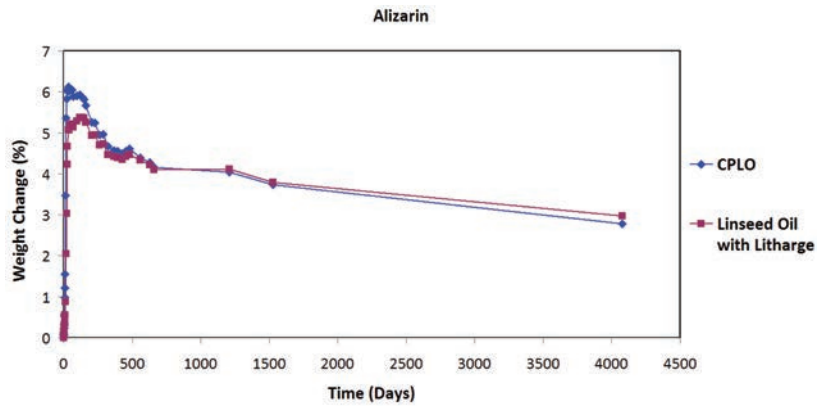


FIGURE 3. Weight changes for two alizarin paints similar to those in Figure 2.

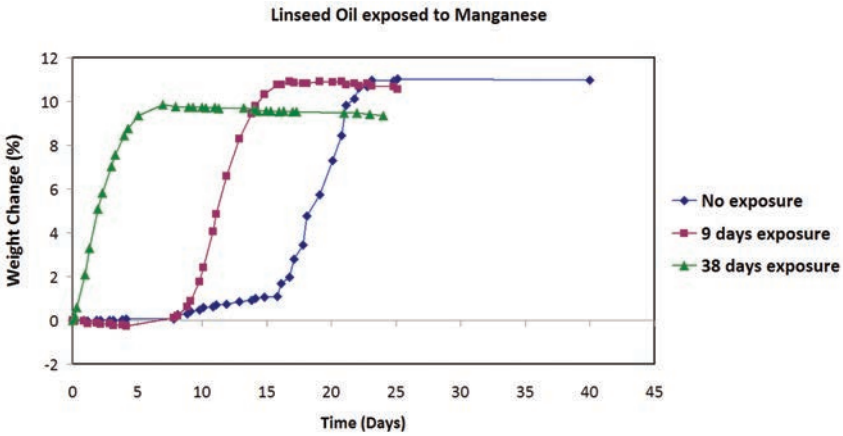


FIGURE 4. Changes in drying time of a cold-pressed linseed oil in contact with solid manganese dioxide for specified periods of time.

continues for years after the paint film has dried. However, both alizarin paints have similar weight changes, unlike the equivalent red iron oxide paints.

The initial autoxidation reaction can be induced to occur faster by the addition of certain metal ions, such as lead, manganese, and cobalt, generally called catalytic driers. They may be intentionally added or may be introduced as impurities or may be extracted from the pigment in the paint. Only a small amount of a catalytic drier, less than 0.5% by weight, is necessary for it to be effective. On the other hand, secondary driers, i.e., those that form complexes throughout the paint film, need to be present in larger amounts and typically account for over 10% by weight of the paint.

Figure 4 shows the changes in drying time of a cold-pressed linseed oil in contact with a small amount (15 mg) of solid manganese dioxide. Linseed oil, because of its increased acidity as hydrolysis progresses, is capable of partly dissolving the manganese dioxide. As contact time increases, more manganese ions will be dissolved and migrate into the oil. The manganese ions then accelerate the drying properties of the oil. This shows the influence of the acidity of the oil on its reaction with pigments and the ability of ions to diffuse into oils. A well-known example is the rapid drying behavior of oils mixed with a raw umber from Cyprus known to contain significant amounts of manganese dioxide. Drying oils may appear to be inert, but because of autoxidation and hydrolysis they become reactive and are able to corrode metals such as copper over time.

Metal substrates, such as copper and lead, will also react with the oils' acidity and dissolve in sufficient amounts, influencing their drying time. Figure 5 plots differences in drying time of the same oil applied to metal surface. This shows again that diffusion of metal ions can influence drying.

Finally, slow-drying paints can be made to dry faster by applying them over a quicker-drying paint or an accelerating substrate. The behavior of a slow-drying alizarin paint in cold-pressed linseed oil applied over different substrates, ranging from an inert one to a copper plate and a lead paint, as well as with a catalytic drier, is shown in Figure 6.

The alizarin paint dries very quickly when placed on a copper substrate and slightly more quickly than cold-pressed linseed oil when placed on a previously dried lead white paint surface. The drying of the paint alone over an inert substrate and paint with a lead drier added is also shown for comparison. One of the puzzling results in this study was that the drying of alizarin paint over lead white was not accelerated as expected and reacted practically identically to that of the alizarin paint by itself. Furthermore, the paint in linseed oil with litharge had a delayed drying, and this could be related to the weight losses observed for these paints (see Figure 2).

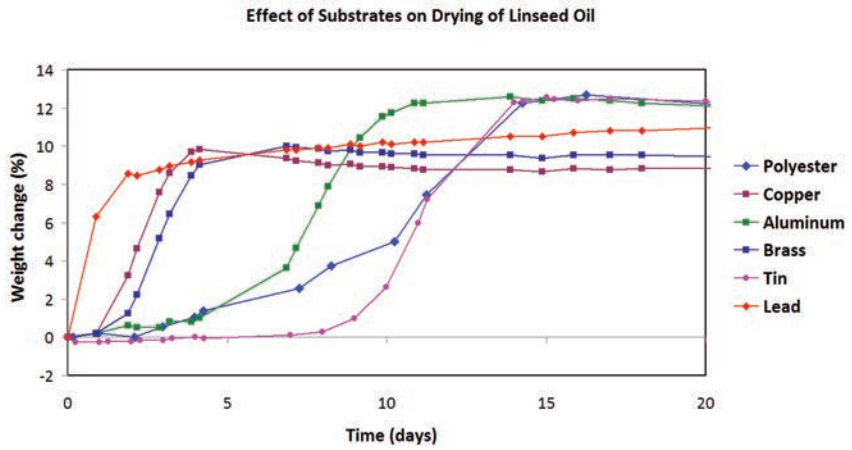


FIGURE 5. Substrate effect on the drying behavior of cold-pressed linseed oil.

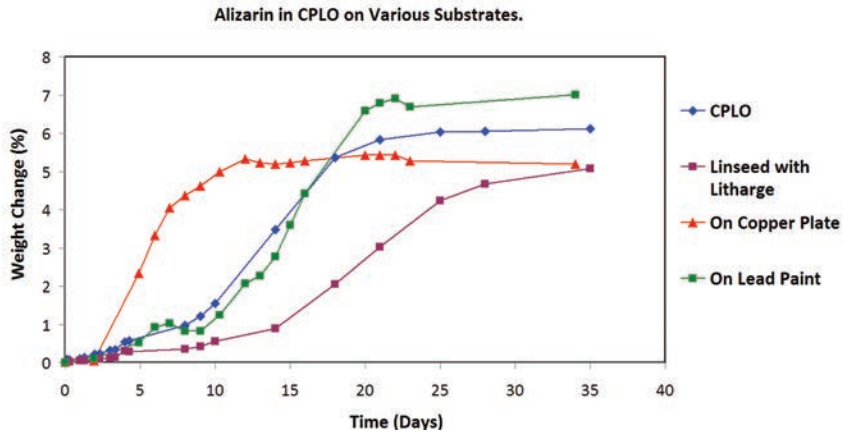


FIGURE 6. Drying behavior of a series of alizarin paints in cold-pressed linseed oil applied on: an inert surface, a copper metal plate, and a lead white paint. For comparison, the paint in linseed oil with a lead drier is also shown.

HYDROLYSIS

In some paints hydrolysis occurs early, whereas after centuries, as for classical paintings, hydrolysis has been measured to have occurred to nearly 90% (Erhardt et al., 2001). The loss of almost three bonds per glycerin ester must have a significant effect on the structure of the oil paint. In order to investigate the effects of the total loss of ester bonds, paints were made with completely hydrolyzed oil and mixtures mimicking oil with 25%, 50% and 75% hydrolysis. These oils were mulled with various pigments to mimic old paints, that is, highly hydrolyzed ones.

The hydrolysis of drying oils frees fatty acids from their esters, and these acids can react with substrates or pigments. The autoxidation process can also produce small chain acids, and oxidation at the C9 position of the unsaturated acids can result in the formation of azelaic acid, found in the analysis of almost all oil paintings (Mills and White, 1987:26–40; van den Berg, 2002).

As a consequence of hydrolysis, large amounts of free fatty acids capable of migrating and/or reacting are created. Figure 7 shows a burnt umber paint that was prepared with partly hydrolyzed linseed oil and therefore has a high concentration of saturated fatty acids. Since these cannot cross-link, they are segregated into nodules in the paint film after several months. Although this burnt umber film is an extreme case, partially hydrolyzed paint films may exhibit similar defects.

This phenomenon can also occur in commercial oil paints, as is shown in Figure 8. A 32-year-old commercially prepared cadmium red oil paint developed a significant white efflorescence on the surface over time as a result of the segregation of the free fatty acids that was therefore easily removed with organic solvents.

METAL IONS

There is an initial time lag before oil paint films begin to take up oxygen, called the induction period. Since this may be rather long for some oils, attempts have been made to shorten it. As mentioned, certain metals, such as lead, cobalt, copper, and manganese, will decrease the drying time if dissolved in small quantities in the oil, as will certain pigments added to the paint. Another way of decreasing the drying time of an oil or paint is to apply it over a layer of paint that does dry quickly, particularly one containing the metal ions mentioned. Consequently, metal

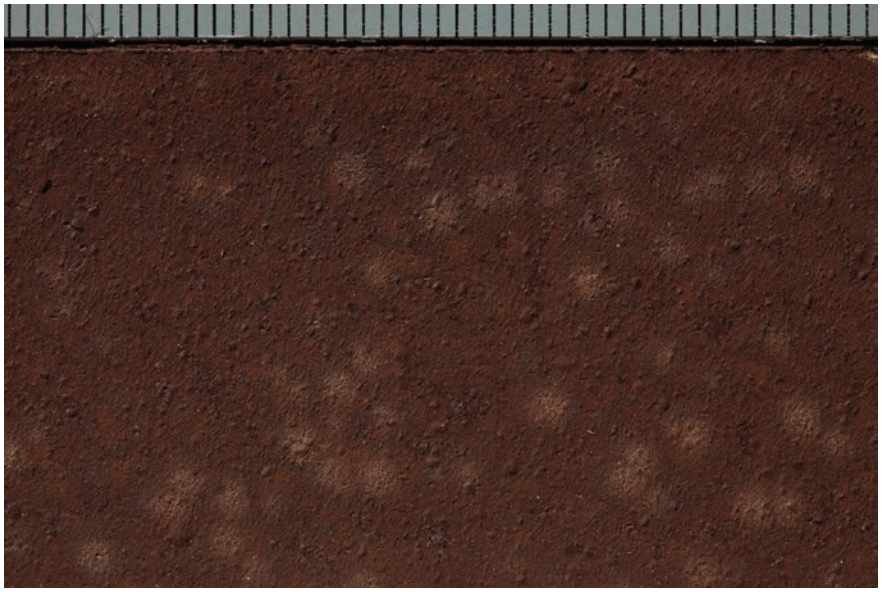


FIGURE 7. Formation of nodules of free fatty acids in a burnt umber paint film after several months. Scale above is in millimeters.

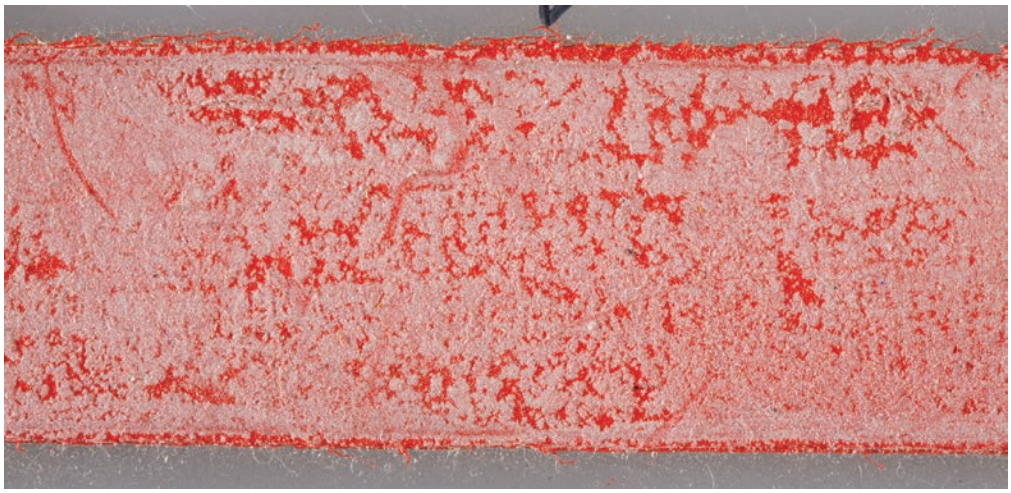


FIGURE 8. Appearance of a 32-year-old commercial cadmium red oil paint. The paint strip is 20 mm wide. The surface is covered with a white efflorescence from the segregation of the free fatty acids.

ions were introduced into paints intentionally, such as by addition of driers, or unintentionally, by dissolution from added pigments or impurities. These can alter both the drying time and, eventually, the stability of the paint itself. Truly inert materials, that is, those that do not react significantly, will not add to the mechanical behavior of the paints. This can be demonstrated by preparing paints with very inert "pigments," or, rather, fillers that do not significantly alter the properties of the oil film from that of an oil film alone.

The changes in the mechanical properties of paints can be illustrated by the stress-strain plots for different commercial burnt umber oil paints shown in Figure 9. These plots show that increasing amounts of manganese ions lead to increased stiffness. Although small amounts of manganese may be good, larger amounts may not be necessarily better. The absence of manganese ions shows the catalytic effect of this ion in changing the long-term mechanical behavior of the paint.

The addition of inert materials to paint may not have any beneficial effects in itself, but inert materials have been and still are used as fillers to decrease the amount of expensive pigments used. To test their effect, silica, barium sulfate, and calcium carbonate were added to cold-pressed linseed oil. The resulting films, after several years, possessed as little strength as the pure linseed oil and were quite flexible. The ones that developed the least

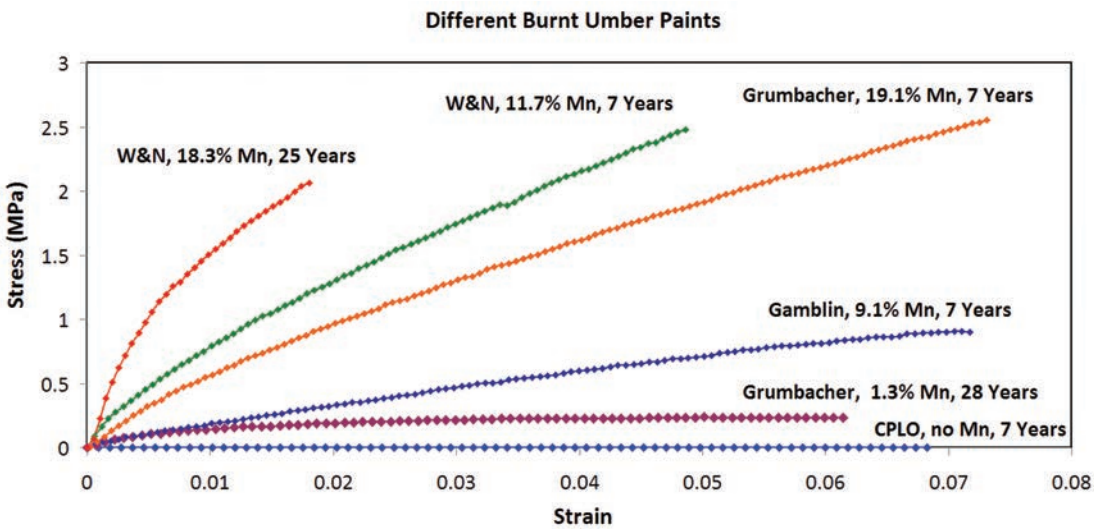


FIGURE 9. Stress-strain plots of commercial umber paints with varying amounts of manganese ions present. The plot for cold-pressed linseed oil without any manganese is added for comparison.

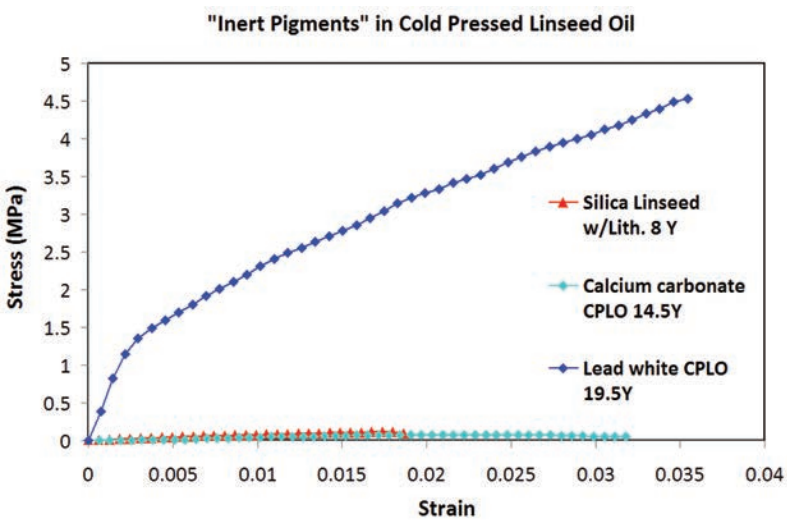


FIGURE 10. Stress-strain plots of "inert" pigments, silica and calcium carbonate in cold-pressed linseed oil. For comparison, the plot of CPLO with lead white is included. The data for the 8-year-old silica in linseed oil with litharge and the 14.5 year barium sulfate in CPLO plot along the abscissa as these films do not develop any mechanical properties.

mechanical properties were the 14.5-year-old barium sulfate in a cold-pressed linseed oil film and the 8-year-old silica in linseed oil with litharge film, and therefore, they are not included in Figure 10, where the stress-strain data of the aged films are shown.

SOLVENTS

The mechanical properties of a paint film depend upon its basic structure and the presence of small organic molecules that may act as plasticizers. The original structure of a paint film contains the ester bonds of the oil and the bonds produced by the cross-linking of the unsaturated fatty acids through autoxidation. The loss of any of these bonds results in weakening the film strength. Any loss of the ester bonds must have a significant effect on the structure of the oil paint. After six years, the paints made with varying degrees of hydrolyzed oil appear as coherent films, but some disintegrate when solvents, such as acetone or toluene, are applied because these solvents can remove the low molecular weight compounds that contribute to the stability of the paints.

Solvents are not the only means of removing low molecular weight compounds. Heat can help evaporate saturated fatty acids, such as palmitic and stearic acids, and an improperly stored or displayed painting can become embrittled by the loss of these plasticizers. The long-term behavior of oil paints also seems to indicate that a small amount of evaporation of fatty acids

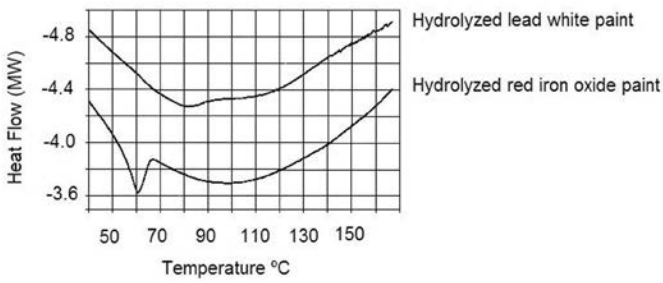


FIGURE 11. Differential scanning calorimetry plot of two paints made with 100% hydrolyzed linseed oil with lead white and red iron oxide pigments, respectively. The peak around 50°C for the red iron oxide paint reflects a phase transition of some fatty acid that does not appear in the lead white paint.

occurs over time. Improper temperature on a hot table may do so as well since the volatility of the fatty acids becomes significant above 70°C to 80°C (Erhardt et al., 2000).

Migration of fatty acids, for example, may occur from an area with little binding capability, such as one containing earth colors (iron oxide–based pigments), to an area where with considerable binding, such as one with lead compounds or zinc oxide. The graph shown in Figure 11 is a differential scanning calorimetry plot for two paints made from hydrolyzed linseed oil with lead white and red iron oxide pigments, respectively. Both paints form coherent films, but upon heating, a low melting phase transition in the red iron oxide paint occurs that is absent in the lead white paint. As indicated by the low-temperature phase transition at 50.5°C, this phase should be quite mobile and capable of migration. It is also apparent that lead-containing areas bind that mobile phase since this phase transition is absent in the lead white paint.

Table 1 shows the reactions of selected paints made with 100% hydrolyzed linseed oil and different pigments, such as red iron oxide, burn umber, smalt, and raw umber. These paints mimic the worst case since all the ester bonds are hydrolyzed. The paints were immersed in the solvent for 5 minutes.

Acetone is the most aggressive solvent, to the point that the paints decompose after treatment. The toluene-treated paints were very embrittled and decomposed with the application of mechanical force. Water and hexane, both rather mild solvents, did not affect the paint films. Previously reported treatments of red iron oxide paints made with 25%, 50% and 75% hydrolyzed oil showed that the effects of hydrolysis became significant for paints with over 50% hydrolyzation (Tumosa et al., 2005).

The paint made with lead white and totally hydrolyzed linseed oil would be unaffected by the solvents based on the differential scanning calorimetry data obtained. The smalt was intermediate to the red iron oxide and white lead paints in behavior.

The loss of these low molecular weight compounds, regardless of whether this occurs by evaporation, migration within the paint, or removal by solvents, can embrittle a paint film and promote cracking as well as loss of color saturation (Tumosa et al., 1999; Erhardt et al., 2001).

CONCLUSIONS

In conclusion, early hydrolysis of oils can lead to the formation of free fatty acids that can alter the initial chemistry and mechanical properties of oil paint films. The diffusion of small molecular weight compounds through the films of a painting may be quite extensive, with metal ions influencing drying rates and fatty acid anions (or neutral compounds) affecting stiffness or flexibility as well as forming accretions. Removal of these small compounds by solvents can embrittle a paint film and promote cracking. Loss of these small compounds by any mechanism will also result in a loss of color saturation. However, the nature of these compounds has yet to be determined.

This study has shown that there still are other questions that require answers. For example, the drying of alizarin paint is accelerated if the paint is applied on a copper substrate, but it is practically not influenced when the paint is applied over a lead white paint. Also, alizarin in a linseed oil with litharge showed an unexpectedly slow drying. Furthermore, the presence of inert materials decreases the mechanical properties of the paint films significantly.

TABLE 1. Reaction of paints made with 100% hydrolyzed linseed oil and different pigments after immersion with selected solvents for 5 minutes.

	Solvent			
Pigment	**Acetone**	**Toluene**	**Hexane**	**Water**
Red iron oxide	decomposed	embrittled	coherent	coherent
Burnt umber	decomposed	embrittled	coherent	coherent
Smalt	decomposed	embrittled	coherent	coherent
Raw umber	decomposed	embrittled	coherent	coherent

REFERENCES

Erhardt, D., R. Cunningham, and S. Rasanen. 2001. "Extraction of Material from Oil Paints by Solvents." In *Materials Issues in Art and Archaeology VI*, ed. P. B. Vandiver, M. Goodway, J. R. Druzik, and J. L. Mass, pp. 43–52. Boston: Materials Research Society.

Erhardt, D., C. S. Tumosa, and M. F. Mecklenburg. 2000. Can Artists' Oil Paints Be Accelerated Aged? *Polymer Preprints* 41(2):1790–1791.

Mills, J. S., and R. White. 1987. *The Organic Chemistry of Museum Objects*. London: Butterworths.

Tumosa, C. S., D. Erhardt, M. F. Mecklenburg, and X. Su. 2005. "Linseed Oil Paint as Ionomer: Synthesis and Characterization." In *Materials Issues in Art and Archaeology VII*, ed. P. B. Vandiver, J. L. Mass, and A. Murray, pp. 25–31. Materials Research Society Symposia Proceedings 852. Boston: Materials Research Society.

Tumosa, C. S., J. Millard, D. Erhardt, and M. F. Mecklenburg. 1999. "Effects of Solvents on the Physical Properties of Paint Films." In *Preprints 12th Triennial Meeting ICOM Lisbon*, ed. J. Bridgland, pp. 347–352. London: James & James.

van den Berg, J. D. J. 2002. *Analytical Chemical Studies on Traditional Linseed Oil Paints*. pp. 9–52. Amsterdam: Molart (FOM).

The Influence of Pigments and Ion Migration on the Durability of Drying Oil and Alkyd Paints

Marion F. Mecklenburg, Charles S. Tumosa, and Edward P. Vicenzi

ABSTRACT. The durability of paints made with drying oil and alkyd mediums refers to their resistance to atmospheric moisture and solvents used in the cleaning of paintings. Ideally, after a reasonable drying period, these paints develop sufficient polymerization and cross-linking to resist swelling and deterioration from most cleaning solvents. Although there has been considerable research on the effects of certain metal ions on the autoxidation of drying oils, that research cannot be used to determine the long-term stability of paints made with drying oils. Current research suggests that a wide variety of metal ions affects the ultimate film formation of oil paints. The exact reaction of those ions with the drying oils is not clearly understood. But there is now considerable evidence that those metal ions are not only capable of migrating throughout a given paint layer but also sufficiently mobile to migrate from one paint layer to an adjacent one in a painting. In this case the migrating ions are capable of either enhancing or degrading the adjacent paint layers. Because artists' alkyd paints contain considerable levels of drying oils, they can react with pigments in an manner analogous to oil paints and therefore will be part of this discussion.

INTRODUCTION

To a practicing painting conservator it can be puzzling that oil paints made with specific pigments, such as organic reds and blacks and some of the earth colors, are easily and safely cleaned on some paintings whereas they are quite sensitive to solvents on others. The question regarding the resistance to damage from cleaning solvents comes down to what enhanced the durability of these paints.

There has been considerable research on the effects of certain metal ions on the autoxidation of drying oils. For example, it has been shown that metal ions such as Co^{2+}, Mn^{2+}, and Fe^{2+} are considered "primary" driers and act during oxidation, whereas Pb^{2+}, Zr^{4+}, and Al^{3+} are "secondary" driers and are active during polymerization. Finally, Ca^{2+}, K^{+}, and Zn^{2+} are considered auxiliary driers as they act to modify the activity of the primary driers (van den Berg, 2002; Tumosa and Mecklenburg, 2005). More importantly, it is generally agreed that the ability of a metal compound to catalyze the oxidation of the oil and form a film depends upon both the solubility and the dissociation of the metal ion in the oil (Olson, 1921; Marling, 1927; Bennett, 1941; Morgan, 1951; Stewart, 1967). In order to get sufficient concentrations of metal ions to catalyze the oxidation of the oil, either the metal ions must be added separately (dissolved or reacted) or the metal ions must dissolve from the pigment itself. Dissociation into metal ions is quite important, and a compound such as tetraethyl lead, which has covalent bonding and does not dissociate, exerts no influence on the drying of oil (Bennett, 1941). The requirement for a metal ion

Marion F. Mecklenburg *and* ***Edward P. Vicenzi****, Museum Conservation Institute, Smithsonian Institution, Museum Support Center, 4210 Silver Hill Road, Suitland, Maryland 20746, USA.* ***Charles S. Tumosa****, Department of Criminology, Criminal Justice and Forensic Studies, University of Baltimore, 1420 North Charles Street, Baltimore, Maryland 21201, USA. Correspondence: Marion F. Mecklenburg, mecklenburgm@si.edu; Charles S. Tumosa, cstchemist@aol.com; Edward P. Vicenzi, vicenzie@si.edu.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

to catalyze the oxidation of the oil is accurate, since unpigmented linseed oil will not form a durable film.

Historically, research on the effects of pigments on paint film formation has been considerably less extensive, with reason. It simply takes a long time to see the actual effects of the pigments on the durability of the paint made with them (van den Berg, 2002). Over the past 30 years, a systematic study of the effects of pigment on the natural drying of oil paints has been conducted. For the past 20 years the paint study at the Museum Conservation Institute of the Smithsonian Institution has included "control paints" specifically manufactured with known pigments, oils, and driers. Some paints are still undergoing modification after 20 years. Some of the results are of interest to those concerned with the preservation of objects containing oil paints.

THE INFLUENCE OF PIGMENTS ON THE MECHANICAL PROPERTIES OF OIL PAINTS

Oil paints made with basic lead carbonate form a remarkably tough and durable film. This paint will continue to change its mechanical properties over a long time, as shown in Figure 1. This figure shows that the white lead paint continues to get stiffer and stronger even after more than 18 years of drying. This is an indication that the paint is still chemically active. This same paint is also fairly resistant to the solvents, as shown in Figure 2, where little change in the mechanical properties of the paint is observed when exposed to water and four different solvents and allowed to dry for 30 days or more.

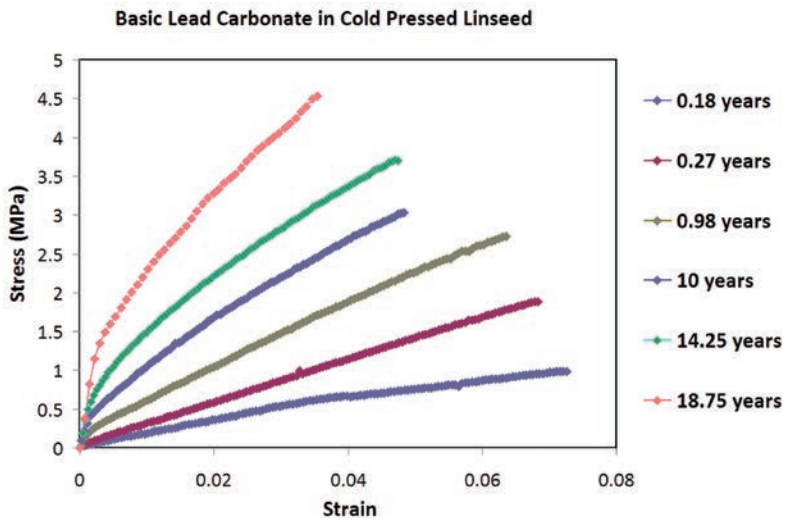


FIGURE 1. Mechanical properties of basic lead carbonate ground in cold-pressed linseed oil. This paint continues to get stiffer and stronger after 18.75 years of drying.

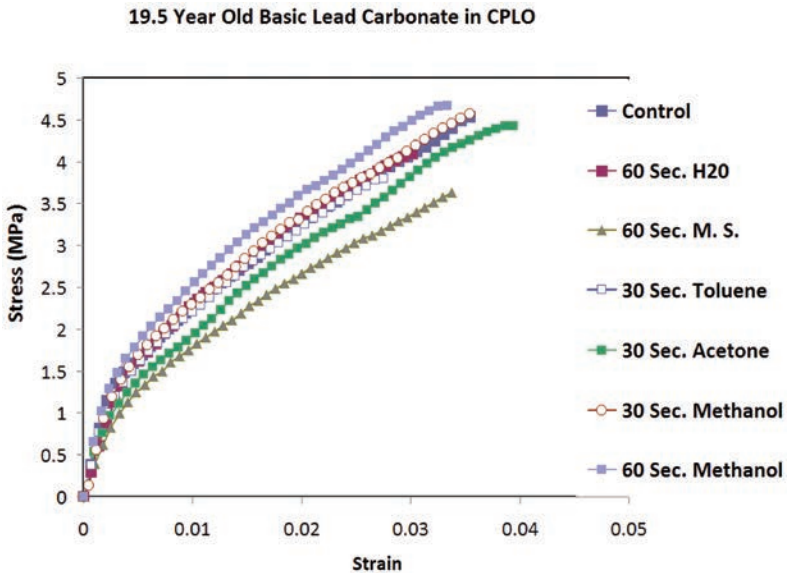


FIGURE 2. Mechanical properties of basic lead carbonate ground in cold-pressed linseed oil (CPLO) before and after being exposed to water and to four different solvents. Any stress-strain plot lower than the control plot is indicative of solvent retention, and this tends to increase the paint's flexibility. This is illustrated by the exposure to mineral spirits (M.S.).

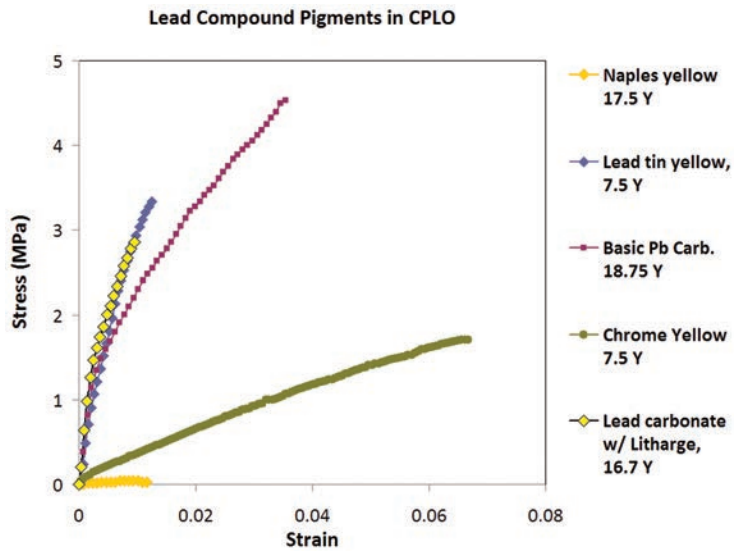


FIGURE 3. Mechanical properties of paints made with cold-pressed linseed oil and five different lead compound pigments. The Naples yellow does not form a durable film even after 17.5 years of drying.

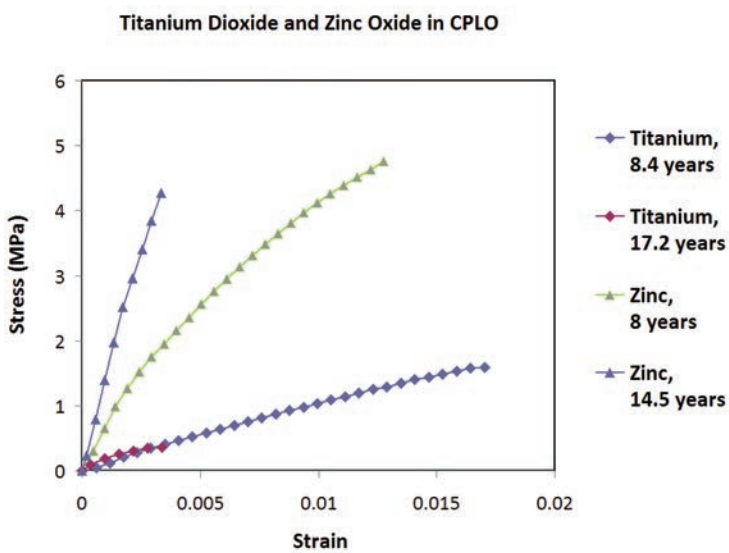


FIGURE 4. Mechanical properties of paints made with cold-pressed linseed oil and zinc oxide and titanium dioxide (rutile). The paint made with the zinc oxide becomes quite brittle, and the paint made with the titanium oxides becomes weak.

However, not all lead compounds form durable paint films. Figure 3 shows the mechanical properties of paints made with cold-pressed linseed oil and five different lead compound pigments. The paints made with lead tin yellow and basic lead carbonate with 1.6% lead monoxide become extremely brittle. The lead compound $Pb(SbO_3)_2Pb_3(Sb_3O_4)_2$, known as Naples yellow, shows very poor film formation. Even after 17.5 years of drying, this paint will completely dissolve in either acetone or methanol after 30 s.

Oil paints made with zinc oxide and cold-pressed linseed oil will become extremely brittle in about three years. They are ultimately capable of delaminating adjacent paint layers made with that pigment and even with other pigments. Paints made with titanium dioxide (rutile) will dry to a very weak paint film. Figure 4 shows the mechanical properties of paints made with titanium dioxide and zinc oxide ground in cold-pressed linseed oil.

Perhaps of greater importance are paints made with the earth colors such as umber, ocher, and Sienna, organic pigments such as alizarin madder, and even cobalt. These will hydrolyze in a very short time, causing the paints to become vulnerable to atmospheric moisture and cleaning solvents (Tumosa and Mecklenburg, 2005). Figure 5 shows the mechanical properties of paints made with cold-pressed linseed oil and the pigments raw and burnt Sienna and raw and burnt umber. Paints made with these pigments appear to develop durable films initially, but as they begin to hydrolyze early in their drying history, they experience a serious loss of mechanical properties such as strength and stiffness as time goes on.

If one of the paints that hydrolyzed is exposed to solvents, the film is seriously altered. Figure 6 shows an 18-year-old raw umber in cold-pressed linseed after drying from a 30 s exposure to acetone. The paint shows distinct cracking in addition to what other changes that may take place.

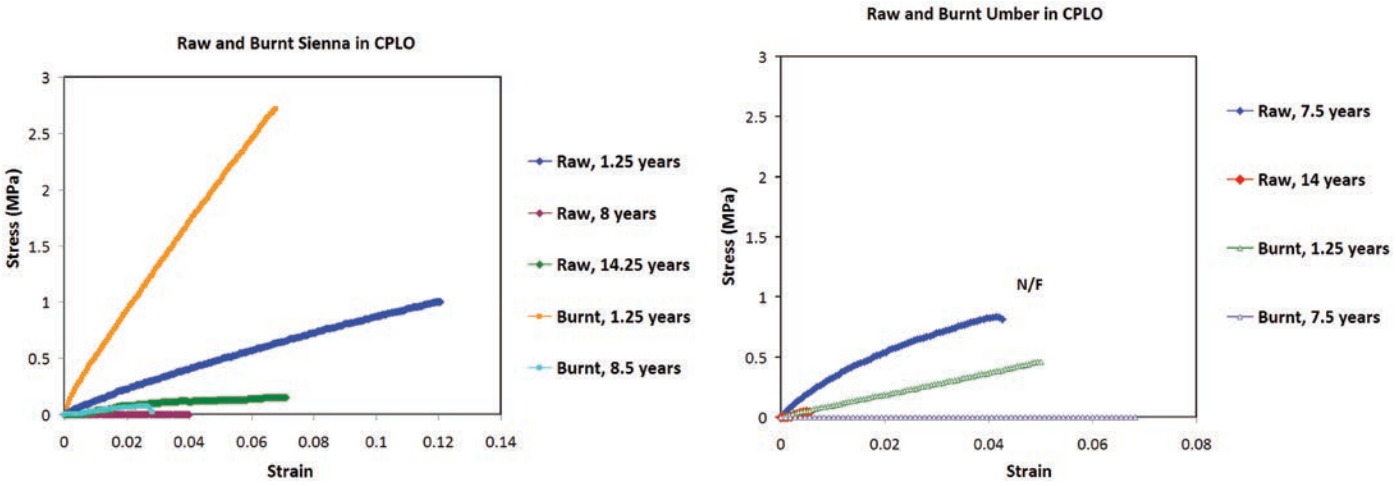


FIGURE 5. Mechanical properties of paints made with cold-pressed linseed oil and the pigments (left) raw and burnt Sienna and (right) raw and burnt umber. The paints made with these pigments appear to develop durable films initially but begin to hydrolyze early in their drying history. N/F indicates that the test was terminated before the sample actually broke.

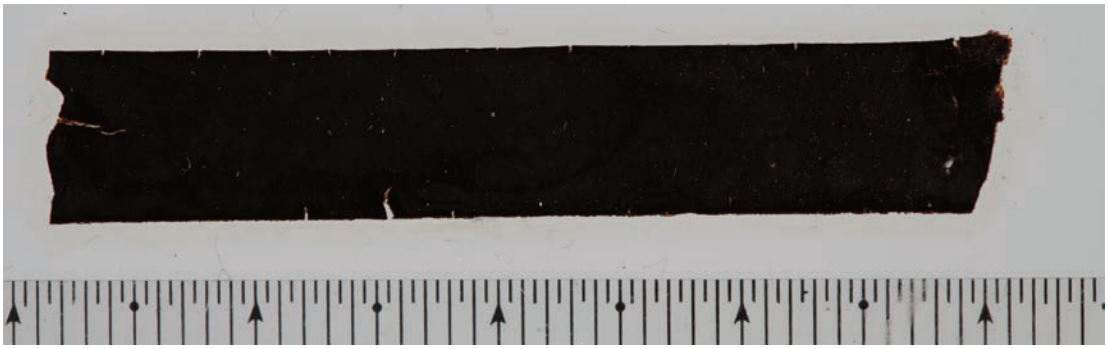


FIGURE 6. An 18-year-old raw umber in cold-pressed linseed after drying from a 30 s exposure to acetone. The cracking will cause loss of stiffness and strength in the paint.

Continued testing of both the mechanical properties of paints and their exposure to solvents leads to the conclusion that resistance to solvents correlates with better mechanical properties. The stiffer and stronger a paint is, the more resistant to solvents it becomes. This is because of the enhanced cross-linking and polymerization. Other paints that show loss of properties after initially appearing to dry normally are yellow ochre, red iron oxide, alizarin madder lake, lamp black, Van Dyke brown, and cadmium yellow.

THE INFLUENCE OF PIGMENTS ON ALKYD PAINTS

It was shown in Figure 4 that zinc oxide will cause an oil paint to become extremely brittle and it was shown that the addition of manganese to burnt umber oil paint can also cause it to turn brittle (Tumosa and Mecklenburgh, this volume). Figure 7 shows the mechanical properties of 7-year-old alkyd paints made with titanium dioxide, cobalt blue, and zinc oxide. The paint made with the zinc has become quite brittle.

Figure 8 shows the mechanical properties of 29-year-old alkyd paints made with titanium dioxide, lead carbonate, titanium dioxide containing zinc oxide, burnt umber containing manganese, yellow ocher, ivory black, and alizarin crimson. The paints containing the zinc oxide, manganese, and lead carbonate become quite brittle, whereas those containing yellow ocher, ivory black, and alizarin crimson remain flexible.

Over time the alkyd paints become more and more resistant to solvents. Figure 9 shows the exposure to solvent has little effect on the mechanical properties of the 29-year-old alkyd paint made with alizarin crimson. It also shows the mechanical

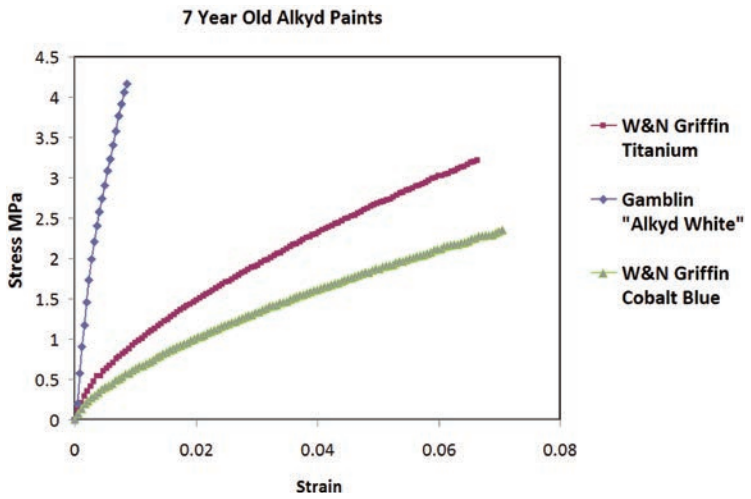


FIGURE 7. Mechanical properties of 7-year-old alkyd paints made with titanium dioxide, cobalt blue, and zinc oxide. The paint with the zinc oxide pigment becomes quite brittle.

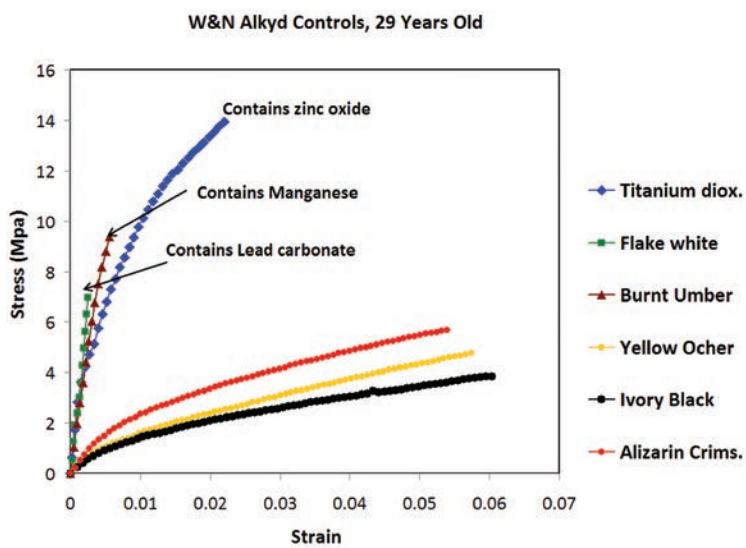


FIGURE 8. Mechanical properties of 29-year-old alkyd paints made with titanium dioxide, lead carbonate, titanium dioxide containing zinc oxide, burnt umber containing manganese, yellow ocher, ivory black, and alizarin crimson. The paints containing the zinc oxide, manganese and lead carbonate become quite brittle.

properties of the alkyd paint when tested after 20 and 29 years of drying and shows that they were still changing. In general, all of the 29-year-old alkyd paints tested and made with yellow ocher, titanium, burnt umber, lead carbonate, alizarin crimson, and ivory black showed considerable resistance to exposure to methanol and acetone.

THE EFFECTS OF MIXING PAINTS ON THEIR MECHANICAL PROPERTIES AND DURABILITY

If an oil paint made with an earth color or an organic pigment is mixed with a lead white paint, the lead contributes to the film-forming process of the mixture, and a durable film can result. This can happen even though the lead paint content comprises less than 25% of the mixture, and it is possible that the concentration of the lead paint could be much smaller and still be effective. Inadvertent or intentional mixing of even small amounts of paint on an artist's pallet might have an effect. In June 2007, three paints, yellow ocher, terre verte, and alizarin madder lake, all ground in cold-pressed linseed oil, were mixed with Grumbacher flake white in alkali-refined linseed oil. The pigments in the flake white are lead carbonate and zinc oxide. The mixtures of the paints were one part white to four parts of the colored paints by volume. The paints were tested after 2.5 years of drying. Figure 10 (left) shows the mechanical properties of the 2.5-year-old mixed yellow ocher paint and pure yellow ocher paints that had dried much longer. The 18-year-old yellow ocher in cold-pressed linseed and the 29-year-old commercial (Speedball) yellow ocher paints hydrolyzed and retained no strength. The 30-year-old commercial (Winsor and Newton) yellow ocher developed some strength, but it is possible that some drier was added to this paint, although none was detected during analysis.

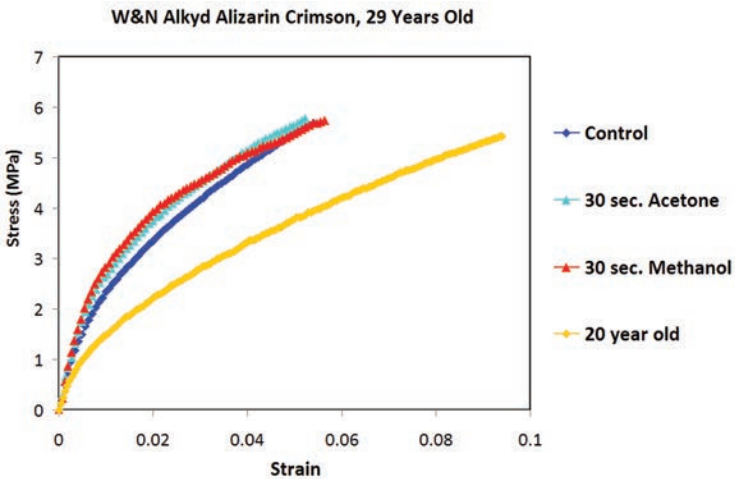


FIGURE 9. Changes in the mechanical properties of an alkyd paint made with alizarin crimson after 20 and 29 years of aging. The effect of solvent exposure of the older paint is also shown. After 29 years of drying the paint is fairly resistant to methanol and acetone.

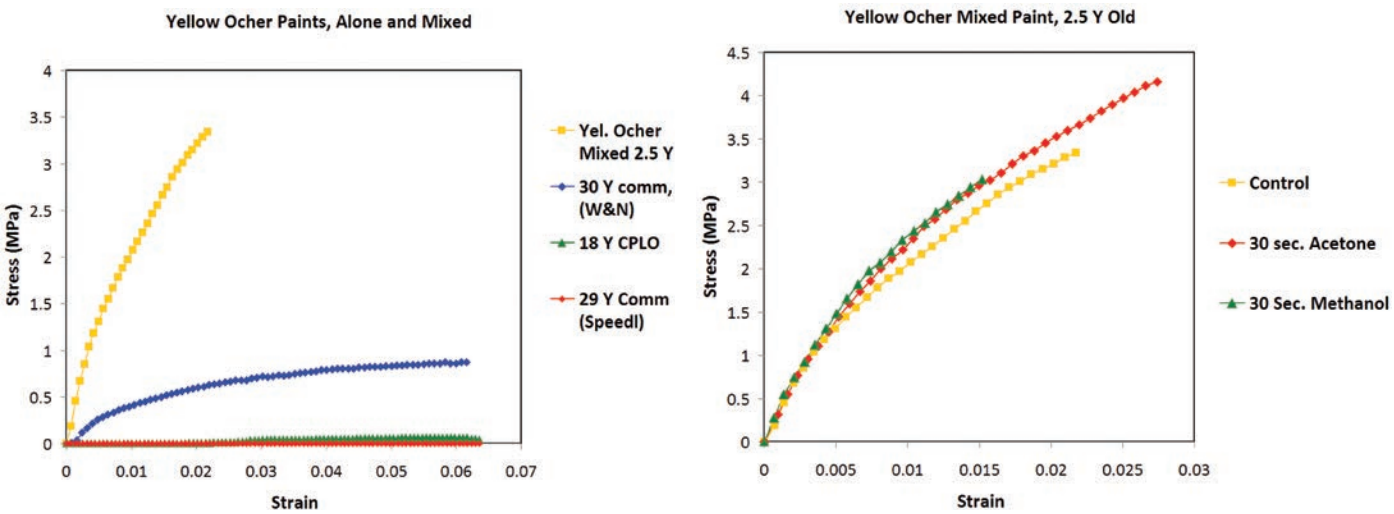


FIGURE 10. (left) Comparison of the mechanical properties of a 2.5-year-old mixed yellow ocher and flake white paint with a pure yellow ocher paint. (right) The effect of solvent exposure on the mechanical properties of the 2.5-year-old mixed yellow ocher paint. After only 2.5 years of drying the paint is fairly resistant to both methanol and acetone.

Figure 10 (right) shows the effects of solvents on the mechanical properties of the 2.5-year-old mixed yellow ocher. There is only a modest degree of stiffening, indicating that unreacted fatty acids were partially removed by the solvents. The paints made with both alizarin and terre verte in cold-pressed linseed oil and mixed with the flake white paint also showed enhanced resistance to solvents.

THE EFFECTS OF ION MIGRATION

Current research suggests that a wide variety of metal ions, apart from the ions mentioned above, affect the ultimate film formation of oil paints. The exact reaction of these ions with the drying oils is not clearly understood, but there is now considerable evidence that some metal ions are not only capable of migrating throughout a given paint layer but sufficiently mobile to migrate from one paint layer to an adjacent paint layer in a painting having multiple layers. In this case, the migrating ions are also capable of affecting the film formation of adjacent paint layers. Unfortunately, this has both positive and negative consequences. On the positive side a painting with a lead white ground has the potential of increasing the durability of all paint layers above the ground. Conversely, paintings with earth grounds do not have the benefit of metal ions contributing to the durability of adjacent layers. Those paintings are typically easily damaged by high environmental moisture levels and cleaning solvents. A layer of paint made with zinc oxide can cause all adjacent paint layers to either

FIGURE 11. Comparison of a 10 s exposure to toluene for (left) an 11-year-old burnt umber on polyester and (right) a 2.5-year-old burnt umber on white lead paint.

become brittle when otherwise they would dry to a tough durable film or alter the drying characteristics of adjacent paint layers to such an extent that "drying cracks" can appear.

In June 2007, six paints (yellow ocher, terre verte, alizarin madder lake, raw Sienna, burnt Sienna, and burnt umber), all ground in cold-pressed linseed oil, were applied over a 16-year-old paint made with basic lead carbonate and cold-pressed linseed oil. The paints were examined after 2.5 years of drying. The first observation that could be made is that the 2.5-year-old paints cast over the white lead paint gained an increased resistance to toluene when compared to the same but older paints cast on polyester films. Figure 11 compares the results of 10 s exposure to toluene on an 11-year-old burnt umber cast on a polyester substrate and a 2.5-year burnt umber cast over the 16-year-old white lead paint. Very similar results were obtained for 10 s exposure to toluene on the yellow ocher, terre verte, alizarin madder lake, raw Sienna, and burnt Sienna cast over the white lead paint. In other words, all of the paints cast over the white lead paint showed a marked increased resistance to the toluene.

X-RAY MICROANALYSIS

In order to confirm that ion migration was occurring in the 2.5-year-old burnt umber paint cast over the 16-year-old lead white paint, X-ray microanalysis was performed on a cross section of this paint. Figure 12 shows the results of this microanalysis, which confirms the presence of lead in the burnt umber layer of paint. It is of interest to note that the iron from the burnt umber did not migrate into the lead paint. Furthermore, spatial simplicity analysis shows that the lead in the white lead paint is lead carbonate, but there is an entirely different lead association forming in the iron bearing burnt umber, as shown in Figure 13.

A multivariate statistical analysis of the hyperspectral X-ray imaging data taken across the burnt umber–white lead interface was performed. Although there are an infinite number of model solutions to such a three-dimensional data cube, the employed

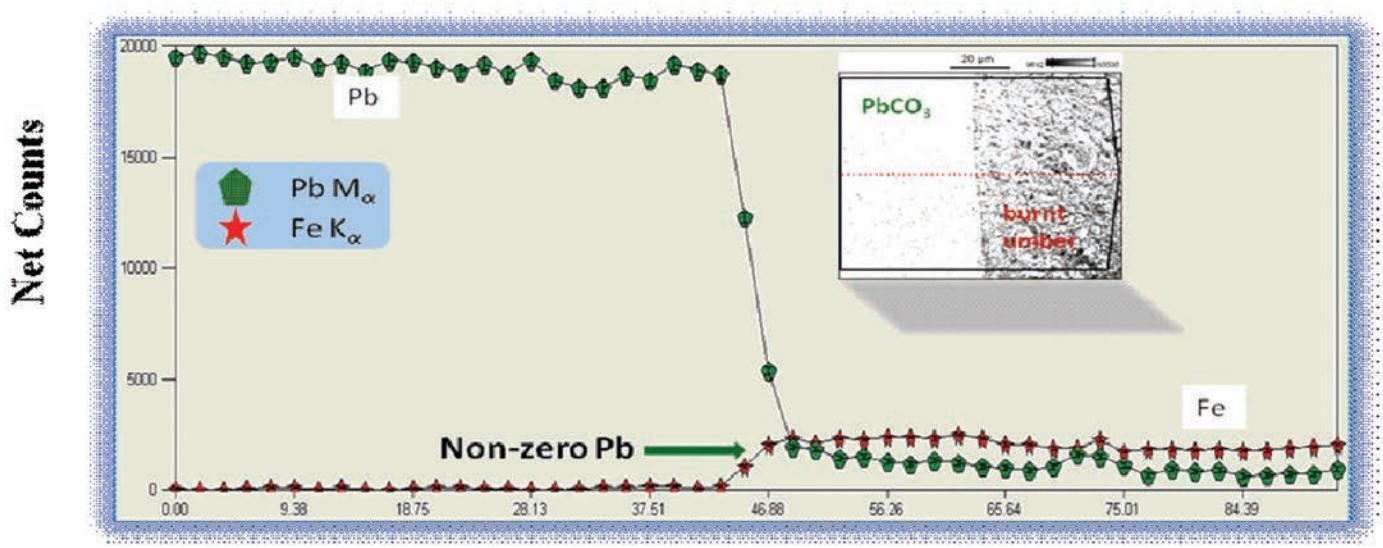


FIGURE 12. The presence of lead in the burnt umber paint is evident, but there is no iron in the lead paint. The inset shows the interface of the two paint layers and the line followed for the analysis.

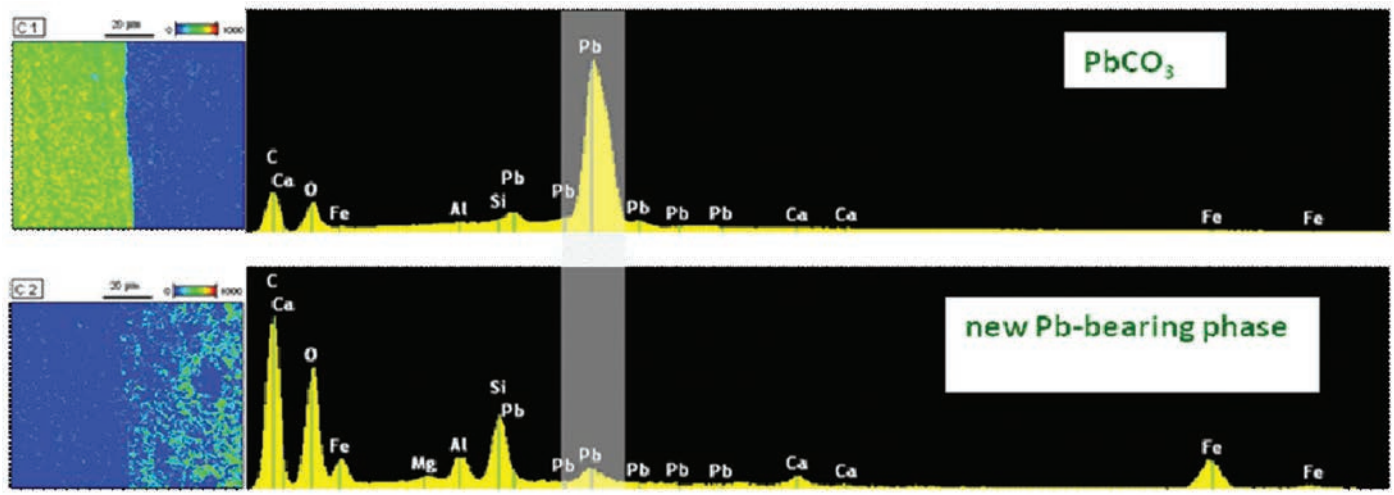


FIGURE 13. (left) Multivariate statistical results approximating the data set by matrix multiplication of pure component concentration images and (right) their spectral signatures. Using a spatial simplicity model, the top image represents $PbCO_3$, and the bottom image corresponds to a new Pb association formed in the umber paint layer (Keenan, 2009).

solution was the one that generates high image contrast in the *X-Y* spatial dimensions (Keenan, 2009). The pure spectral components derived from this analysis include a chemically complex Pb-bearing component rich in C and O as well as containing Mg-Al-Si-Ca and Fe (see Figure 13). The Pb compound extends from the Pb carbonate interface to some tenths of micrometers into the paint layer.

A one-dimensional analysis of the spectral image data additionally supports the presence of Pb well into the paint layer. Integrated net counts (characteristic minus background radiation) for Pb derived from an area at the interface region for the Pb M_a X-ray line are plotted orthogonal to the interface and distinctly show nonzero Pb net intensities within the burnt umber layer (Figure 12).

DISCUSSION

Because lead is not known to be present in burnt umber at any appreciable concentration, an explanation for the Pb-bearing phase within the paint after 2.5 years is best described by cation migration. During the drying process, the basic lead carbonate is apparently solubilized, hypothetically by minor amounts of hydrolyzing oil, at the interface and migrates *via* diffusion into the umber paint layer. The presence of clays in this layer may trap the migrating lead compound to form a spectrally distinct association, as evidenced by the presence of the Si-Al-Mg-Ca. Whether this is merely a physical adsorption, typical of clays, or a new compound that integrates all these elements plus the Pb-Fe-C-O is yet to be determined. Although the exact nature of this phase is currently not known, carbon comprises ~39% (by weight) of its composition, suggesting an oil or fatty acid lead salt plus the ferruginous clay mixture.

The possibility has been considered that the Pb signal detected is an artifact caused by secondary characteristic fluorescence of Pb in Pb carbonate by characteristic Ca and Fe radiation in the burnt umber. However, considering the low concentration of Ca in the paint and the large offset in energies between the Fe *K* line and Pb *M* X-ray lines, these possibilities appear remote. Secondary fluorescence of Pb by continuum radiation in the paint layer is perhaps more likely. However, the distribution of the Pb-bearing phase is not concentrated at the interface and tails- off in intensity as a function of distance, as one might expect if this phenomenon were responsible for producing the Pb spectral signature observed. Moreover, the 1-D profile of Pb net intensities do not decrease sharply as a function of distance from the Pb carbonate interface, further suggesting that evidence for cation migration during the drying process has been established.

CONCLUSIONS

The results obtained from this long term study can be summarized as follows:

- The early drying of oil paints is due to autoxidation, but it does not necessarily result in a tough, durable film.
- The later film-forming processes are largely the result of metal ions from pigments, added driers, or even contamination from other materials inducing cross-linking and polymerization.

- Not all pigments contribute to the development of good paint films, and some, such as zinc oxide, can actually have detrimental effects, causing brittleness and even delaminating the paint layers.
- Pigments such as the earth colors, organic dyes, and blacks fail to induce a durable film, and this is a result of hydrolysis of the paints.
- Without pigments supplying "active" metal ions, film formation in drying oils is poor.
- Different pigments have dramatically different effects on film formation and the durability of both oil and alkyd paints.
- In the competing processes of polymerization, cross-linking, and hydrolysis, hydrolysis can be dominant in paints made with many pigments, including the earth colors.
- Mixing paints made with active pigments can increase the durability of paints with less active pigments.
- One layer of paint in a painting can affect other adjacent layers both positively and adversely. The paint chosen for the ground layer can affect the long-term stability of the painting.

This study has confirmed that ion migration occurs and has shown that this migration may result in the formation of new associations for the case of a burnt umber paint applied over a lead white paint. Research into the ion migration process is just beginning, and far more research is required to elucidate it.

REFERENCES

Bennett, E. F. 1941. *A Review of Driers and Drying*. Brooklyn, N.Y.: Chemical Publishing Co.

Keenan, M. R. 2009. Exploiting Spatial-Domain Simplicity in Spectral Image Analysis. *Surface and Interface Analysis*, 41:79–87.

Marling, P. E. 1927. Accelerators and Inhibitors of Linseed Oil Drying. *Canadian Chemistry and Metallurgy,* 11:63–66.

Morgan, H. H. 1951. Cobalt and Other Metals as Driers in the Paint and Allied Industries. *Paint Manufacture,* 21:239–248, 259.

Olson, J. 1921. Cobalt and Its Compounds. *Monthly Digest National Varnish Manufacturers' Association,* 17:2–12.

Stewart, W. J. 1967. "Driers." In *Treatise on Coatings*. Volume 1: *Film-Forming Compositions*, ed. R. R. Myers and J. S. Long, part 1, pp. 211–223. New York: Marcel Dekker.

Tumosa, C. S., and M. F. Mecklenburg. 2005. The Influence of Lead Ions on the Drying of Oils. *Reviews in Conservation*, 6:39–47.

van den Berg, J. D. J. 2002. Analytical Chemical Studies on Traditional Linseed Oil Paints. Ph.D. thesis, University of Amsterdam, Amsterdam.

Effects of Organic Solvents on Artists' Oil Paint Films: Swelling

Alan Phenix

ABSTRACT. This paper concerns the sensitivity of artists' oil paints to organic solvents. Specifically, it examines the respective capacities of single organic solvents and mixtures of solvents to cause swelling as a consequence of sorption into the paint and solvency action thereupon. The swelling power of a solvent is essentially an indicator of its relative strength in terms of action on the original (oil) paint material. The paper collates and interprets the large body of experimental data that has been gathered on the solvent-induced swelling of two particular reference oil paint samples. These samples comprise uniform films prepared from mixtures of proprietary yellow ochre and flake white tube paints, one portion being artificially aged by exposure to high-intensity daylight and the other portion not light aged. The method adopted for measuring swelling employed a combination of low-power stereomicroscopy and quantitative image analysis. The initial output from the swelling experiments is a series of swelling curves for each solvent that shows the mean percentage change over time in area ΔA % for the group of paint fragments of the particular sample type tested. Various approaches are explored to correlate the respective swelling powers of individual solvents with a range of solvency descriptors and physicochemical constants.

INTRODUCTION: BACKGROUND AND CONTEXT

Organic solvents rightly remain an important class of chemical tools used by conservators in the cleaning of paintings, particularly for removing aged varnishes and overpaints; and as with all tools, a proficient practitioner must understand how they work in order to be able to use and control them with skill and refinement. The respective effects of organic solvents on varnishes and original paint are key elements in the theoretical and technical frameworks that conservators use to comprehend the cleaning process, to assess the risks and benefits of cleaning, and to diagnose and solve the practical problems presented by specific objects requiring treatment.

This study focuses on the sensitivity of artists' oil paints to organic solvents. It has long been recognized that swelling of the oil binder represents an important aspect of risk in the cleaning of paintings using solvents. If the paint is swollen to a significant degree, it becomes softened and its capacity to bind pigment may be diminished, possibly to the point where the pigment is vulnerable to erosion by the mechanical action of the cleaning swab. Safety in cleaning depends to a large degree on controlling the magnitude and rate of paint swelling. In contrast to the phenomenon and risk factor of leaching (i.e., the extraction of soluble, low molecular weight components of the organic binder phase), which are arguably more notional or abstract concerns for it is improbable that a conservator performing the operation of cleaning could actually *sense* any organic molecules that are

***Alan Phenix**, Getty Conservation Institute, 1200 Getty Center Drive, Suite 700, Los Angeles, California 90049, USA. Correspondence: aphenix@getty.edu.* *Manuscript received 19 November 2010; accepted 24 August 2012.* *Copyright © 2013 The J. Paul Getty Trust. All rights reserved.*

being extracted or gauge their amount. Swelling is a direct, tangible phenomenon that conservators can to some degree detect and test for in advance of beginning the actual cleaning treatment. Pronounced swelling of the paint is usually indicated by pigment being picked up on a solvent-laden swab. The ultimate swelling power of a solvent is essentially an indicator of its relative "strength" in terms of action on the original (oil) paint material.

The framework for solvent selection in varnish removal that was developed by Hedley (1980) has stood for many years as the basis of technical and theoretical foundations of solvent cleaning within painting conservation (Banik and Krist, 1984; Cremonesi, 2000; Pietsch, 2002). Using the Teas fractional solubility parameter chart and selected swelling data from Stolow (1963), Hedley identified for oil paint a "peak swelling region," which represented a zone of solvent power associated with increased risk in varnish removal and cleaning. However, despite its longstanding prevalence within conservation, it must be accepted now that the Hedley-Stolow model for oil paint–solvent interactions has some important practical and theoretical limitations that have a bearing on its reliability as a guide to paint sensitivity. These limitations derive both from the intrinsic shortcomings of the Teas factional solubility parameter system and from the choice of the particular paint swelling data (on paint prepared from linseed *stand* oil) from which the peak swelling region was deduced (Phenix, 1998, 2002b). A common problem encountered by the practicing conservator is the discrepancy between the swelling data presented by Stolow (1963) and the insights into the comparative activity of solvents that comes from experience of cleaning paintings.

REEVALUATING THE SOLVENT-INDUCED SWELLING OF ARTISTS' OIL PAINTS: EXPERIMENTAL METHOD

Set against the contextual background just described, in the early 2000s experimental studies were undertaken to reevaluate the solvent-induced swelling of artists' oil paints (Phenix, 2002b, 2003). The method adopted for measuring swelling was a combination of low-power stereomicroscopy and quantitative image analysis (Phenix, 2002a): swelling was monitored by measuring changes in the in-plane area of multiple small fragments of paint over time during the course of immersion in solvent. With some technical refinements, this method has been subsequently applied to other oil and alkyd paints by Zumbühl and coworkers, with comparable results (Zumbühl, 2005; Fuesers and Zumbühl, 2008).

The purpose of the present paper is to collate and interpret the large body of swelling data that has been gathered on two particular reference oil paint samples that have been studied in depth. These paint samples, referred to as type 16 and type 17, are uniform films prepared in 1991 from proprietary yellow ochre and flake white tube paints (Winsor & Newton Artists' Oil Colours) mixed 1:1 by weight, with added dry pigment (also 1:1 by weight) to increase the pigment volume concentration; see Phenix (2002b:65) for the full details of these paint samples. Paint films 16 and 17 are identical except that type 17 was artificially aged by exposure to a high dose of UV-filtered natural daylight. Within a large group of differently pigmented paint samples that were tested in the initial phase of this project, paints 16 and 17 were identified as being intermediate in their swelling behavior and were selected for in-depth study primarily on the basis of this characteristic. The swelling responses of these paints have now been measured in a total of more than 80 pure solvents and 45 solvent mixtures. It should be stressed that many of the solvents tested in this study were selected on the basis of particular chemical or physicochemical properties. Their inclusion in this study does not imply their suitability for the cleaning of paintings. The majority of data forming the basis of this present analysis have been reported previously (Phenix, 2002b, 2003), but some additional swelling results are included here on paint type 17 exposed to selected additional solvents and mixtures.

RESULTS AND DISCUSSION: REFLECTIONS ON THE SWELLING RESPONSES OF PAINT TYPES 16 AND 17

The initial output from the swelling experiments is a series of swelling curves for each solvent that shows the mean percentage change over time in area ΔA % for the group of fragments of the particular paint sample tested. Typical responses are illustrated in Figure 1 for paint types 16 and 17 exposed by immersion to a range of hydrocarbon solvents. It can be seen immediately that the different solvents each cause different swelling responses in the paints, varying both in the rate of swelling and in the maximum or equilibrium magnitude of swelling, the latter property (ΔA_{max} %) being a reflection of the magnitude of solvent activity on the paint. For both paint films, the maximum or equilibrium degree of swelling ΔA_{max} % increases in the following sequence: *iso*-octane, white spirit (17% aromatics), turpentine, xylene, and toluene, a pattern reflective of increasing polarity and solvent power. For paint type 16, swelling curves obtained for two other aromatic solvents, ethylbenzene and diethylbenzene, are also shown in Figure 1A; both of these solvents cause lower degrees of swelling than toluene and xylene, and slower rates of swelling. Similar patterns of swelling response within the different chemical classes of solvent (alcohols, ketones, esters, etc.) are discussed in Phenix (2002b).

The time taken for the swelling to reach half the value of maximum or equilibrium degree of swelling $t_{½}$ (minutes) has been taken as a single numerical indicator for the *rate* of swelling. Again, it can be seen immediately that the two aromatic solvents toluene and xylene cause quite rapid swelling compared to the nonaromatic solvents: for paint type 16, $t_{½}$ values are 3.5 and 3 minutes, respectively. Some general trends can also be observed by comparing the respective swelling effects of the solvents on paints 16 and 17: in all of the cases shown in Figure 1, the light-aged paint film 17 swells to a lower ultimate degree and more slowly than paint 16. Correlations of the two primary indicators of swelling response, ΔA_{max} % and $t_{½}$, for all solvents tested with

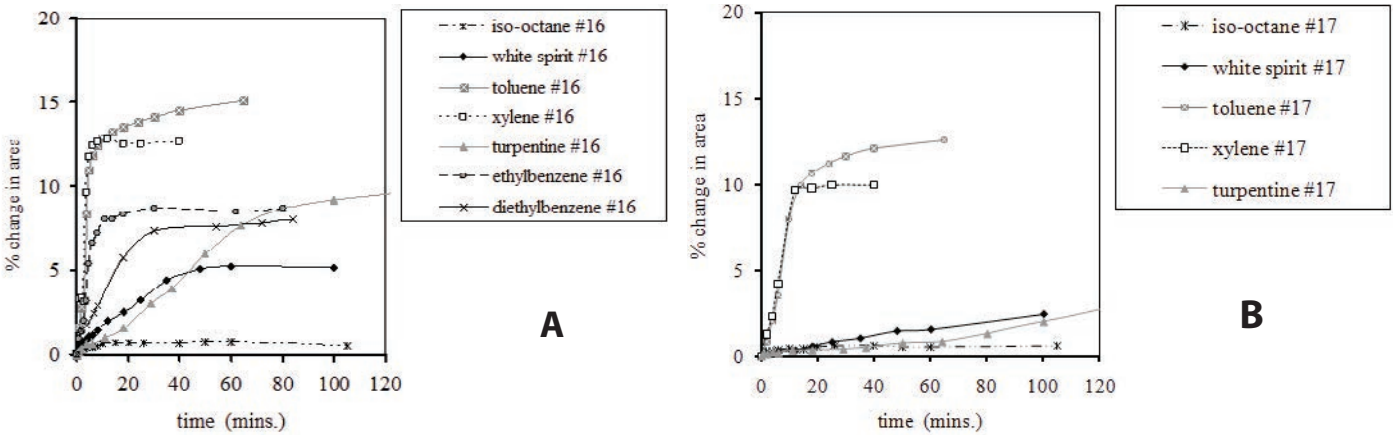


FIGURE 1. Representative swelling curves of paint films (A) 16 and (B) 17 in selected hydrocarbon solvents.

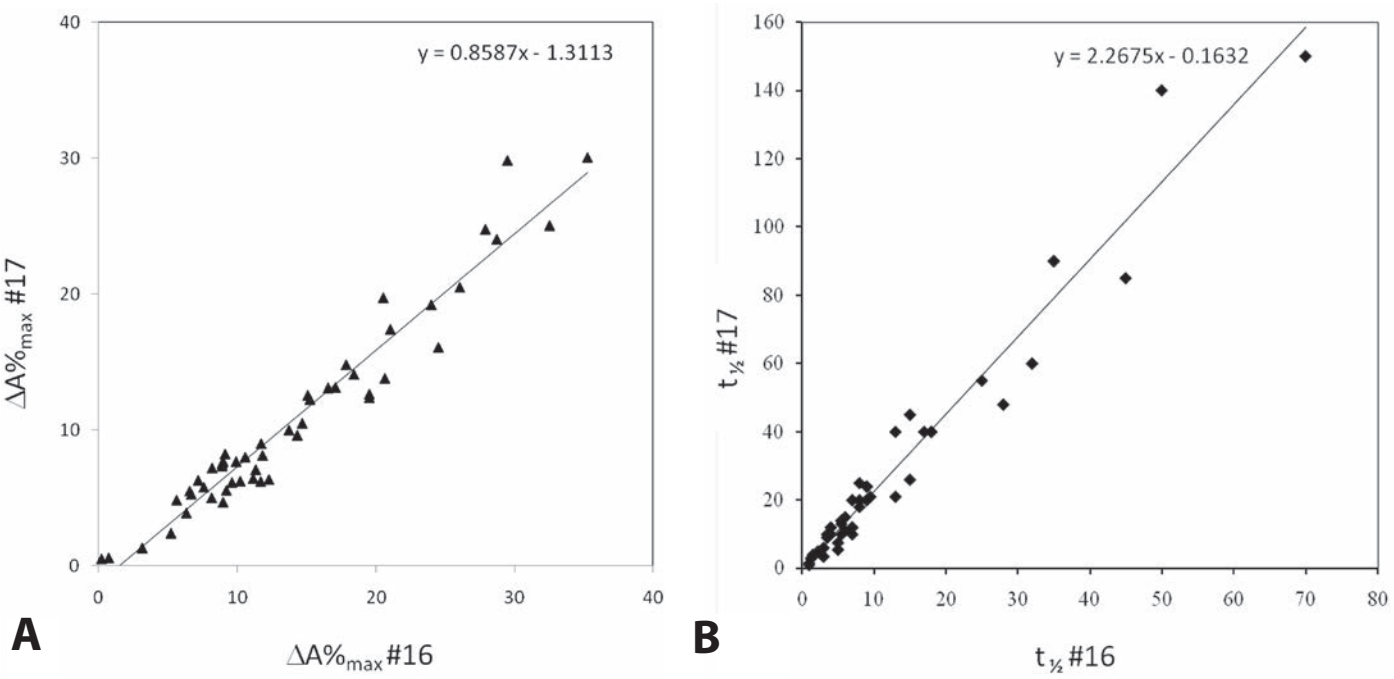


FIGURE 2. Correlation of (A) ΔA_{max} % and (B) $t_{½}$ values for paint films 16 and 17.

both paint types 16 and 17 produced generally linear relationships (Figure 2A,B): the light-aged paint, type 17, swelled more slowly and to a lesser degree than paint 16 (not light aged).

Plotting the values of maximum or equilibrium degree of swelling ΔA_{max} % for paint 16 as a function of solubility parameter ∂ (Figure 3) results in a pattern that has some superficial similarities to the data presented by Stolow (1963). Solvents of low polarity and cohesiveness, such as the aliphatic hydrocarbons, show low values of ΔA_{max} %. Increasing ∂ leads generally to increased swelling; chloroform (trichloromethane, ∂ = 19.5 MPa^{½}) and cyclohexanone (∂ = 19.7 MPa^{½}) produced very high degrees of swelling (ΔA_{max} % of 32.5% and 39.6%, respectively), a finding that is broadly consistent with the results of Stolow (1963). But rather than the progressively declining relationship of swelling power to solubility parameter in the ∂ range above ~20 MPa^{½} that was reported by Stolow, it can be seen from Figure 3 that solvents

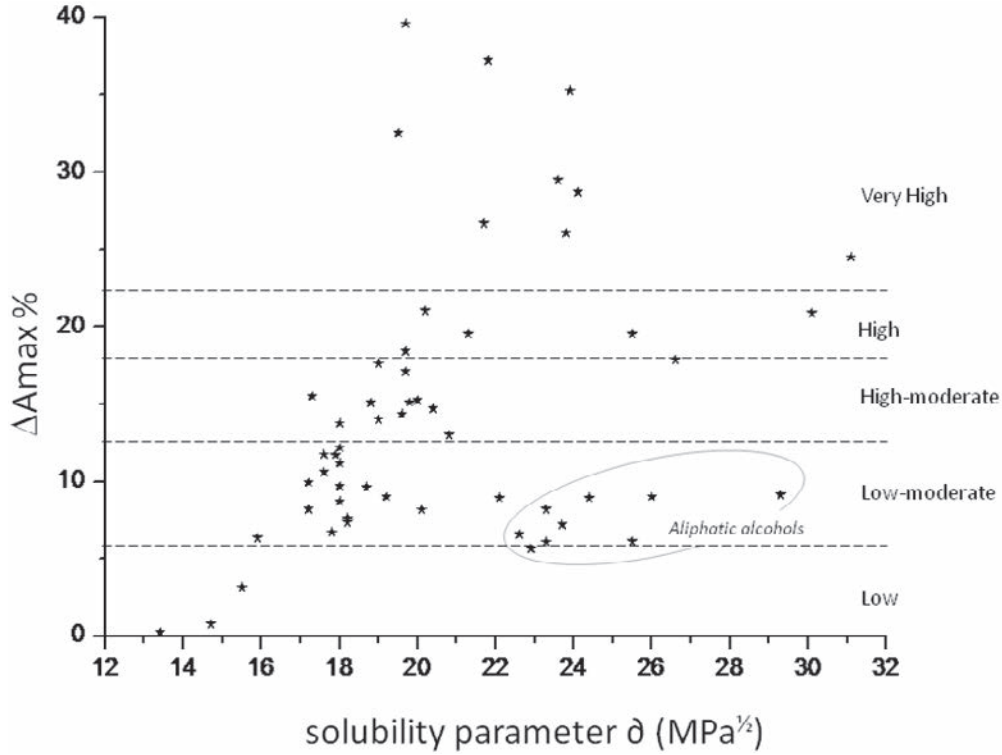


FIGURE 3. Maximum or equilibrium swelling ΔA_{max} % of paint film 16 as a function of solvent solubility parameter δ, showing arbitrary classification of solvents into swelling power categories. The δ values are mostly from Marcus (1999).

with high values of ∂ (>22 MPa$^{1/2}$) vary significantly in their swelling action. Some of the high-∂ solvents produce high and, in some cases, very high levels of swelling: this group of solvents generally comprises high-polarity solvents that would be immediately recognized by conservators as being very "active" on oil paint, such as benzyl alcohol, *N*,*N*-dimethyl formamide (DMF), *N*-methyl-2-pyrrolidone (NMP), pyridine, morpholine, and other high-polarity liquids that are sometimes referred to as "super solvents", such as 2,2,2-trifluoroethanol. Another cluster of high-∂ solvents (those contained within the oval in Figure 3), however, induced only low to moderate degrees of swelling: this group of solvents comprises the lower aliphatic alcohols, including cyclohexanol.

One of the key outcomes of the earlier interpretations of this body of swelling data was a general descriptive vocabulary for solvents in terms of their activity on oil paint, as reflected by the ΔA_{max} % values obtained for paint types 16 and 17 (Phenix, 2002b). Five broad arbitrary categories of "swelling power" were defined in terms of ΔA_{max} %, as described in Table 1 and illustrated in Figure 3. Likewise, solvents were classified into five groups according to rate of swelling as reflected by their $t_{½}$ values (Table 1). Accordingly, a solvent such as acetone (paint 16: ΔA_{max} % = 8.9%, $t_{½}$ = 1.25 minutes; paint 17: ΔA_{max} % = 7.6%, $t_{½}$ = 3 minutes) would be classed as very fast and low-moderate in terms of swelling power; on the other hand, a solvent like benzyl alcohol (paint 16: ΔA_{max} % = 26%, $t_{½}$ = 32 minutes; paint 17: ΔA_{max} % = 21%, $t_{½}$ = 60 minutes) would be classed as slow and very high swelling power.

TABLE 1. Classification of solvents by swelling power ΔA_{max} % and rate of swelling $t_{½}$

Category	Paint type 16	Paint type 17
Classification of solvents by swelling power ΔA_{max} %		
Low swelling	<6	<4
Low-moderate	6–12	4–9
High-moderate	12–18	9–15
High swelling	18–22	15–21
Very high	>22	>21
Classification of solvents by rate of swelling $t_{½}$ (minutes)		
Very slow	≥50	≥100
Slow	20–50	40–100
Intermediate	8–20	20–50
Fast	3–8	6–20
Very fast	≤3	≤6

Another key finding of this work was that the groups of solvents consisting of aliphatic alcohols (methanol, ethanol, propan-1-ol, etc.), aliphatic acyclic ketones (acetone, butanone, etc.), and the lower aliphatic esters (*n*-butyl acetate, ethyl propanoate, etc.) generally fell within the class of low-moderate swelling power. Since these solvents are common staples for practical varnish removal, this finding should be somewhat reassuring to most practitioners who rely heavily on these solvents. By the same token, it must be recognized that oil paint may still be very sensitive to solvents that fall into the low-moderate swelling category and possibly even some of those in the low swelling group.

The initial interpretation of the swelling data obtained on paints 16 and 17 (Phenix, 2002b) consciously avoided using the Teas chart because of the now well-established, intrinsic theoretical shortcomings of the Teas fractional solubility parameter system (Phenix, 1998). Plotting the complete set of swelling results (ΔA_{max} % values) obtained for paint 16 in pure solvents and solvent mixtures, categorized as in Table 1, highlights some of the difficulties with this mode of graphic representation. It becomes apparent immediately that the area of special sensitivity of oil paints to solvents is appreciably more complex than the single zone of high swelling suggested by Hedley (1980). Solvents capable of causing significant degrees of swelling, for example, those having ΔA_{max} values of 12% or greater for paint 16 (high-moderate, high, and very high swellers), are spread over a large part of the Teas chart, covering a broad range of polarities, extending from the aromatic hydrocarbons and apolar mixtures of ethanol and white spirit through the chlorinated solvents (Teas fractional dispersion force parameter (f_d) values of ~60–70) to the strongly dipolar solvents such as the amides and cellosolves (f_d values of ~40–50). The areas of low and low-moderate swelling (ΔA_{max} < 12%) correspond mostly to the aliphatic hydrocarbons, aliphatic acyclic ethers, aliphatic alcohols, aliphatic acyclic ketones, and some of the esters (Figure 4).

Rather than the single zone of highly active solvents represented by the Hedley-Stolow peak swelling region, it can be seen now that high and very high swelling solvents and solvent mixtures lie in several zones across the Teas chart. One of the more significant observations on the results as a whole, when presented using the Teas fractional solubility parameter diagram, is that scattered between and very close to the zones corresponding to high-moderate, high, and very high swelling pure solvents and solvent mixtures, there are several solvents that cause just low-moderate swelling on the paint film tested. These isolated regions of low-moderate swelling arise from the fact that the aliphatic acyclic ketones and the aliphatic acyclic esters populate the central area of the active part of the Teas chart, between about f_d = 48 and 65, yet the aliphatic acyclic ketones and esters are just low-moderate swellers compared to the high- or high-moderate swelling solvents all around. This anomaly reflects some of the limitations of the Teas fractional solubility parameter chart: solvents from families with quite different solubility properties, for example, ketones and amides, are clustered close together in similar regions of the chart. Solvents having similar Teas solubility parameters can have very different swelling powers: compare, for example, acetone (f_d = 47, f_p = 32, f_h = 21; $\Delta A_{max} \approx 9\%$) with *N*-methyl-2-pyrrolidone (f_d = 48, f_p = 32, f_h = 20; $\Delta A_{max} \approx 30\%$). Irregularities such as this, which become even more evident when considering mixtures of solvents, illustrate the limitations of the Teas fractional solubility parameter diagram as a reliable map for safer cleaning practice, to the extent that in the eyes of some "this system is not an adequate tool for restorers" (Zumbühl,

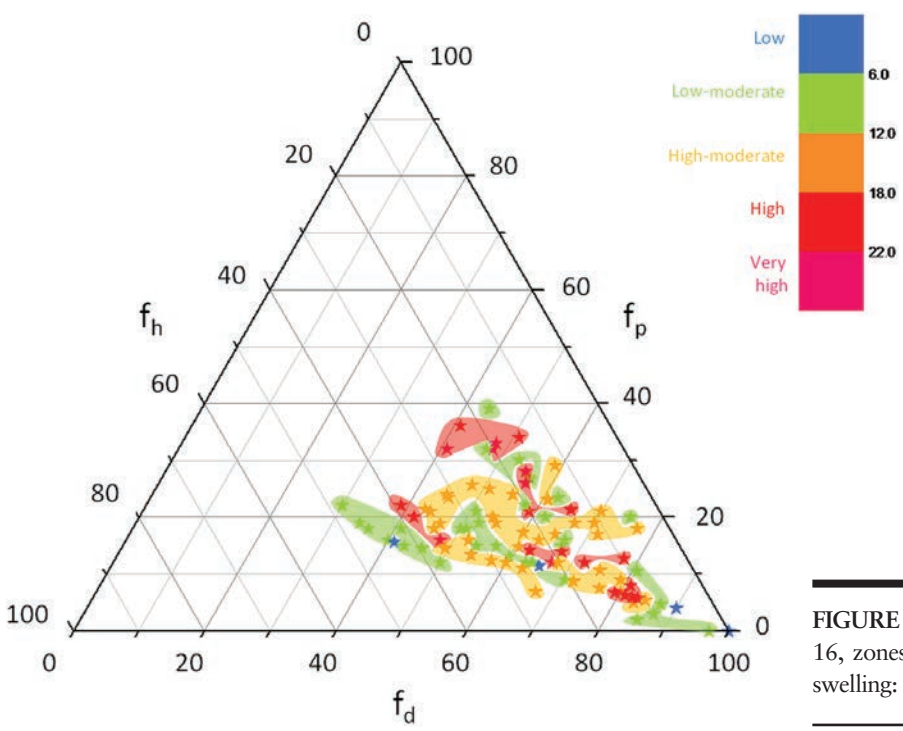


FIGURE 4. Teas solubility diagram, showing for paint type 16, zones corresponding to different degrees of maximum swelling: pure solvents and solvent mixtures.

2005:262). Put another way, it might be said that the Teas fractional solubility parameter system does not clearly reveal the particular chemical and/or physicochemical factors that contribute to the swelling action of any given solvent.

A FEW OBSERVATIONS CONCERNING MIXTURES OF SOLVENTS

It has been known since the earliest investigations of solvent-induced swelling of oil paints that binary mixtures of solvents, typically those consisting of a polar and a nonpolar substance (such as hydrocarbons with ethanol or acetone), generally cause greater degrees of swelling than the individual pure solvents. This phenomenon was demonstrated again for paints 16 and 17 immersed in mixtures of ethanol and white spirit (Phenix, 2002b:85): even relatively small additions of ethanol to white spirits resulted in significant increases in the ultimate degree of swelling.

As noted earlier, the swelling of paints 16 and 17 has been measured for a total of more than 45 solvent mixtures, including some established cleaning formulations. Perhaps the most dramatic finding of the enhanced activity of binary mixtures compared to the pure solvents has been observed with one of the series of aliphatic ester: dimethyl sulfoxide (DMSO) mixtures were proposed as cleaning solvents in Italy about 10 years ago, specifically, progressively increasing proportions of DMSO in ethyl or *n*-butyl acetate (Cremonesi, 2000:102). Figure 5 shows, for the light-aged paint type 17, the variation in maximum or equilibrium swelling as a function of volume proportion of DMSO with *n*-butyl acetate. It is recognized that mixtures of DMSO and ethyl acetate are generally preferred to ones with *n*-butyl acetate on the grounds of greater volatility. However, the ethyl acetate mixtures could not be reliably tested using the experimental method adopted because of bubble formation, which interfered with the quantitative image analysis.

Two main points can be deduced from this set of data. First, it can be seen again that even small additions (<5% v/v) of DMSO to *n*-butyl acetate dramatically increase the swelling power of the solvent. Second, the magnitudes of swelling generated in paint 17 by DMSO:*n*-butyl acetate mixtures containing greater than 5% v/v DMSO are very high indeed: the series of mixtures 5:95, 10:90, 20:80, 30:70, 40:60, and 50:50 DMSO:*n*-butyl acetate represent the six most active liquids of the entire range tested in these studies (Figure 5). Notwithstanding any other concerns over retention of solvent (i.e., DMSO), it should be recognized that these mixtures are extremely powerful in their (swelling) action on oil paints.

ALTERNATIVE DESCRIPTORS OF SOLVENCY CHARACTERISTICS

It is almost universally recognized now that a wide range of chemical and physicochemical factors have a bearing on the specific interactions that occur between a solvent and solute and that these interactions cannot be reliably described by the dispersion force-polar force/hydrogen bond approaches of Teas and its nonfractional precursor, Hansen. It is worth noting briefly here other particular approaches to solvent description and classification that have established a degree of enduring currency within the field of solvency science (Phenix, 1998; Marcus, 1999; Reichardt, 2003). One is the use of various physicochemical constants (including volume V_m, boiling point, refractive index n_D, dipole moment μ, and dielectric constant ε) and empirical parameters of polarity, of which Reichardt's solvatochromic polarity scales E_T30 and E_T^N are perhaps the most widely used. The second is

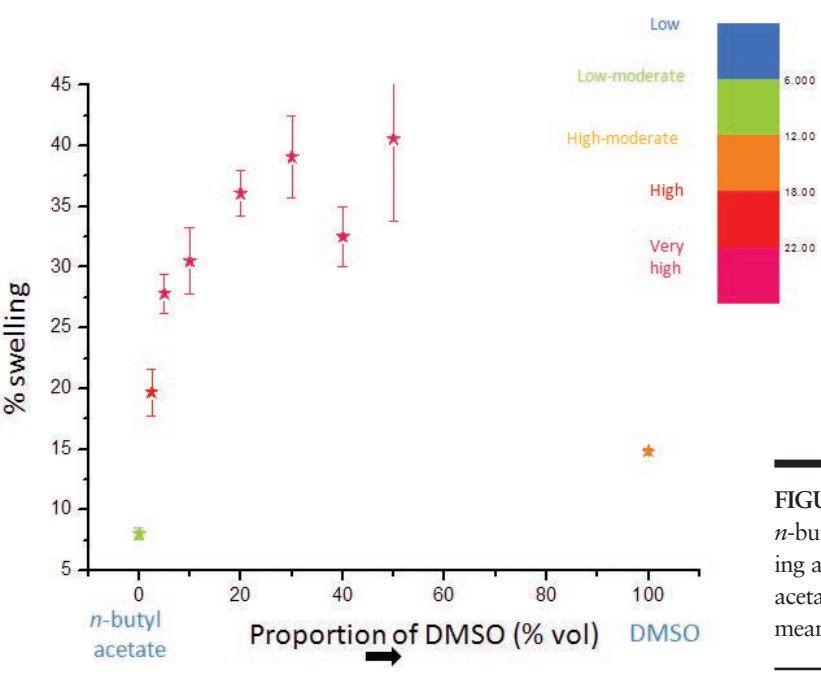


FIGURE 5. Swelling of paint type 17 in mixtures of DMSO and *n*-butyl acetate and variation in maximum or equilibrium swelling as a function of volume proportion of DMSO with *n*-butyl acetate. Error bars represent the standard deviations for each mean value of ΔA_{max}%.

another solvatochromatic system, the three-parameter α, β, π^* system of Kamlet, Abboud, Taft (KAT) and coworkers in which α is a scale of hydrogen-bonding donor acidity, β is a scale of hydrogen-bonding acceptor basicity, and π^* is an index of solvent polarity and polarizability. Given that so many factors and chemical characteristics influence solubility behavior, the major recent developments in classification and description of solvents and in modeling solubility behavior have involved multivariate statistical analytical methods, including multiple linear regression analysis and principal component analysis (Gramatica et al., 1999; Reichardt, 2003:84–91). Both of these statistical analytical methods have been applied to the data set of maximum or equilibrium swelling values ΔA_{max} % against a variety of physicochemical constants and solubility parameters with a view to investigate the relative importance of individual variables in determining the data structure. The multivariate statistical analyses were performed with The Unscrambler version 9.7 software by Camo (http://www.camo.com/) using the data set of swelling results for paint type 16 and the range of solvents for which the most solubility parameters and physical constants were known; the analyses were carried out both on the original raw data and on the original data set after centering and scaling. A full description of the multivariate analyses conducted on the data set is beyond the scope of this paper; however, for the present purposes, it is sufficient to report that partial least squares regression analysis found no quantitative correlations between the dependent X variables (i.e., the solubility parameters and physical constants) and the independent Y variable (the actual measured response, i.e., ΔA_{max}). Principal component analysis was more informative: using all three of the KAT parameters (α, β, π^*) with Reichardt normalized polarity E_T^N, molar volume V_m, and refractive index n_D as limited variables, it was established that the most influential variables across five principal components were the KAT parameters, β in particular, followed by π^* (or E_T^N), plus V_m and n_D. A ternary plot of β against π^* and n_D (Figure 6A) shows improved discrimination in the clustering of solvents according to their swelling power and solvent class compared to solubility parameter approaches based on dispersion, polar, and hydrogen-bonding forces (Teas and Hansen). The binary plot of β against π^* (Figure 6B) shows the strong dependence of swelling power in relation to these two parameters. It can be seen that high-moderate, high, and very high swelling solvents generally lie in

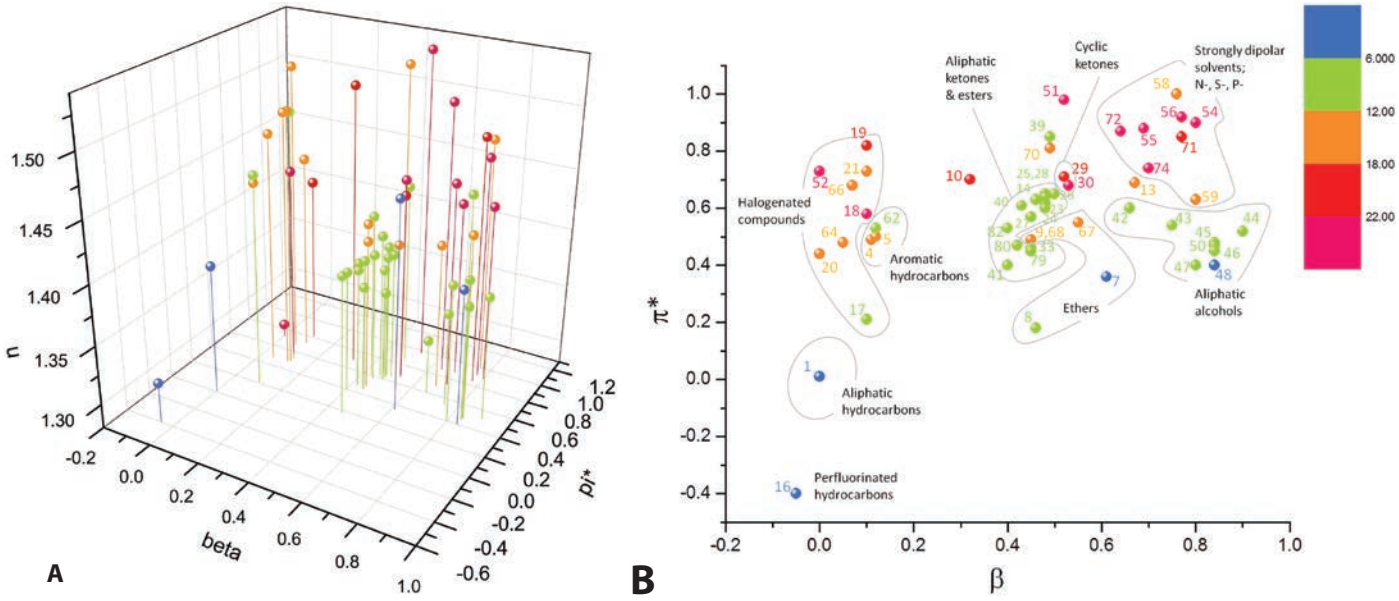


FIGURE 6. (A) Ternary plot showing swelling of paint type 16 in pure solvents as a function of Kamlet, Abboud, and Taft parameters β and π^* and refractive index n. (B) Binary plot showing swelling of paint type 16 in pure solvents as a function of Kamlet, Abboud, and Taft parameters π^* and β. Key to solvents in (B): 1 = 2,2,4-trimethylpentane (*iso*-octane); 4 = toluene; 5 = xylene (mixed isomers); 7 = 1,8-cineole; 8 = di-*n*-butyl ether; 9 = 1,4-dioxane; 10 = anisole; 13 = methoxy propanol; 14 = methoxypropyl acetate; 16 = perfluorodecalin; 17 = tetrachloromethane; 18 = chloroform; 19 = dichloromethane; 20 = 1,1,1-trichloroethane; 21 = 1,2-dichloroethane; 23 = acetone; 24 = butanone; 25 = methyl isopropyl ketone; 26 = pentan-2-one; 27 = pentan-3-one; 28 = methyl *iso*butyl ketone; 29 = cyclopentanone; 30 = cyclohexanone; 33 = *n*-butyl acetate; 39 = g-butyrolactone; 40 = ethyl acetoacetate; 41 = diethyl carbonate; 42 = methanol; 43 = ethanol; 44 = propan-1-ol; 45= propan-2-ol; 46 = butan-1-ol; 47 = butan-2-ol; 48 = 2-methyl-propan-1-ol; 50 = cyclohexanol; 51 = benzyl alcohol; 52 = 2,2,2-trifluoroethanol; 54 = N-methyl formamide; 55 = DMF; 56 = NMP; 58 = DMSO; 59 = tributyl phosphate; 62 = ethyl benzene; 64 = trichloroethylene; 66 = chlorobenzene; 67 = tetrahydrofuran; 68 = *n*-amyl acetate; 70 = acetophenone; 71 = 2-pyrrolidone; 72 = pyridine; 74 = morpholine; 79 = ethyl acetate; 80 = ethyl propanoate; 82 = propyl acetate.

two regions: $\beta < 0.32$ and $\beta > 0.52$. In the range of β values between ~0.32 and ~0.52, most solvents, mainly aliphatic ketones, esters, and ethers, are low-moderate swellers, as are solvents with $\beta > 0.62$ and $\pi^* < 0.60$, which are the aliphatic alcohols.

CONCLUSIONS

This study has demonstrated that the interaction of organic solvents with artists' oil paints to cause swelling is more complex than the existing models (Stolow, 1963; Hedley, 1980) suggest and that the complexity of this interaction is not faithfully described using the Teas fractional solubility parameter diagram approach. It has been found that better discrimination of the swelling power of solvents can be achieved using other descriptors, of which the KAT parameters (α, β, π^*), Reichardt normalized polarity E_T^N, molar volume V_m, and refractive index n_D appear the most significant. Similar interpretation of the swelling action on oil paints of *mixtures* of solvents remains an outstanding task, but productive lines of enquiry will probably lie in the use of empirically determinable descriptors, such as Reichardt polarity (E_T30, E_T^N), which can be applied to mixtures as well as pure solvents (Reichardt, 2003:425–428; Bosch and Rosés, 1992; Catalán et al., 2000). Finally, and perhaps most usefully for the practicing conservator, this work has offered a broad descriptive vocabulary for the respective actions of different organic solvents and mixtures in terms of ultimate swelling power (ΔA_{max} % values) and rate of swelling ($t_{½}$ values).

Acknowledgments

Special thanks go to Emma Richardson, GCI postdoctoral fellow, for assistance with multivariate statistical analysis of the swelling results.

REFERENCES

Banik, G., and G. Krist. 1984. *Lösungsmittel in der Restaurierung.* [Solvents in Conservation.] Vienna: Verlag der Apfel.

Bosch, E., and M. Rosés. 1992. Relationships between E_T Polarity and Composition in Binary Solvent Mixtures. *Journal of the Chemical Society, Faraday Transactions,* 88(24):3541–3546. http://dx.doi.org/10.1039/ft9928803541.

Catalán, J., C. Díaz, and F. García-Blanco. 2000. Characterization of binary solvent mixtures. *Journal of Organic Chemistry,* 65:9226–9229. http://dx.doi.org/10.1021/jo001008u.

Cremonesi, P. 2000. *L'uso dei solventi organici nella pulitura di opere policrome.* [The Use of Organic Solvents in the Cleaning of Polychrome Objects.] Padua: Il Prato.

Fuesers, O., and S. Zumbühl. 2008. "The Influence of Organic Solvents on the Mechanical Properties of Alkyd and Oil Paint." Paper presented at 9th International Conference on NDT-Art 2008, Jerusalem, Israel. http://www.ndt.net/article/art2008/papers/219Fuesers.pdf. (accessed 3 December 2012).

Gramatica, P., N. Navas, and R. Todeschini. 1999. Classification of Organic Solvents and Modelling of Their Physico-chemical Properties by Chemometric Methods Using Different Sets of Molecular Descriptors. *Trends in Analytical Chemistry,* 18(7):461–471. http://dx.doi.org/10.1016/S0165-9936(99)00115-6.

Hedley, G. 1980. Solubility Parameters and Varnish Removal: A Survey. *The Conservator,* 4:12–18. http://dx.doi.org/10.1080/01410096.1980.9994931.

Marcus, Y. 1999. *The Properties of Solvents*. Chichester, UK: John Wiley.

Phenix, A. 1998. Solubility Parameters and the Cleaning of Paintings: An Update and Review. *Zeitschrift für Kunsttechnologie und Konservierung,* 12(2):387–409.

———. 2002a. The Swelling of Artists' Paints in Organic Solvents. Part 1, A Simple Method for Measuring the Inplane Swelling of Unsupported Paint Films. *Journal of the American Institute for Conservation,* 41:43–60. http://dx.doi.org/10.2307/3179896.

———. 2002b. 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.

———. 2003. The Swelling of Artists' Paints by Organic Solvents and the Cleaning of Paintings: Recent Perspectives, Future Directions. In *Postprints of Annual Conference of the American Institute for Conservation, Paintings Specialty Group, Miami, June 2002,* ed. H. Mar Parkin, pp. 71–86. Washington, D.C.: American Institute for Conservation.

Pietsch, A. 2002. *Lösemittel: Ein Leitfaden für die restauratorische Praxis.* VDR-Schriftenreihe zur Restaurierung 7. Stuttgart, Germany: Theiss Verlag.

Reichardt, C. 2003. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed. Weinheim, Germany: Wiley-VCH.

Stolow, N. 1963. Application of Science to Cleaning Methods: Solvent Action Studies on Pigmented and Unpigmented Linseed Oil Films. In *Recent Advances in Conservation*, ed. G. Thomson, pp. 84–88. London: Butterworths.

Zumbühl, S. 2005. Illusion mit System. Das Lösemitteldreieck in der Praxis. Aspekte zur Charakterisierung der Wirkung von binären Lösemittelmischungen. [The Solvent Triangle in Practice. Characterization Aspects of the Effect of Binary Solvent Mixtures.] *Zeitschrift für Kunsttechnologie und Konservierung,* 19(2):253–263.

An Evaluation of Color Change in Nineteenth-Century Grounds on Canvas upon Varnishing and Varnish Removal

Meredith Watson and Aviva Burnstock

ABSTRACT. Color changes in prepared samples of grounds based on those used by Vincent van Gogh were measured before and after varnishing with dammar and artificial aging. Sections of the samples were lined using wax-resin. Varnish was removed using solvents, and practical observations were made about the influence of the ground composition and lining on the reversibility of varnish. Quantitative measurements of color change and qualitative observations made during varnish removal showed that wax-resin lining facilitated varnish removal, whereas varnishing of absorbent grounds was irreversible. Consultations with conservators and treatment reports of paintings cleaned at the Van Gogh Museum, Amsterdam, provided some theoretical context and practical guidelines for the removal of nonoriginal varnishes from Impressionist paintings.

INTRODUCTION

The application of varnish can significantly alter the appearance of paintings. By the mid-1880s many avant-garde French painters chose not to varnish (Swicklik, 1993; Schaefer, 2009; Callen, 2000). Later, Neo-Impressionists and twentieth-century artists relinquished varnishing in favor of a matte aesthetic (Miller, 1983; Jirat-Wasiutynski and Travers Newton, 1998). Following his arrival in Paris in 1886, Vincent van Gogh was influenced by the works of Camille Pissarro, Paul Gauguin, and Emile Bernard, whose preferences for unvarnished surfaces are well known (Hendriks, 2008). For example, notes declaring that the painting was not to be varnished can be found on the reverse of paintings by the Pisarros (Callen, 1994; Schaefer, 2009), and it has been inferred that van Gogh chose to leave many of his paintings unvarnished (Hendriks and van Tilborgh, 2006; Peres, 1990; Schaefer, 2009). Once out of the artists' hands, many paintings were varnished in keeping with academic norms or contemporary taste, rendering them more sellable (Callen, 1994). Most Impressionist and Post-Impressionist paintings have been subsequently varnished, and some have been lined by dealers, collectors, and conservators for protection from dirt and pollutants or in keeping with a preference for the saturated surface (Bruce-Gardner et al., 1987).

The present study focuses on the use of dammar, a natural resin varnish that was used by the conservator J. C. Traas to varnish paintings at the Van Gogh Museum, Amsterdam, in the 1920s and 1930s and was used by dealers and colormen for varnishing paintings in the nineteenth and twentieth centuries. The aims of this study were to provide data on color change in Impressionist grounds on varnishing and subsequent removal of the varnish and to explore, by consultation with experienced conservators of Impressionist

***Meredith Watson**, 3209 West Franklin Street, Richmond, Virginia 23221, USA. **Aviva Burnstock**, Department of Conservation and Technology, Courtauld Institute of Art, Somerset House, London WC2R ORN, UK. Correspondence: Meredith Watson, meredithswatson@gmail.com; Aviva Burnstock, aviva.burnstock@courtauld.ac.uk.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

paintings, some of the practical problems of removing varnish, with the ultimate goal of displaying the works in their original unvarnished condition.

EXPERIMENTAL SAMPLES

The 42 experimental ground samples used in this study were one of three sets prepared as part of the Historically Accurate Reconstruction (HART) project in 2005 and have been stored since their completion at the Rijksdienst voor Cultureel Erfgoed in Amsterdam. The preparation of the samples was based on the results of analyses of the grounds used for paintings by Vincent van Gogh and contemporary historical recipes (Hendriks and Geldof, 2007; Van Bommel et al., 2005). They included a range of canvas and hemp fiber supports, different methods of applying the size layer, and combinations of binding media and inorganic materials. The composition of the samples used in this study is given in Table 1. For a detailed description of the procedures and materials used to make the samples, see Carlyle (2005:85).

In a previous study (Nieder et al., 2011) each sample was wax-resin lined and varnished with dammar in quadrants, illustrated by the example shown in Figure 1. This set of samples was reexamined in the present study following a subsequent campaign of light aging.

LIGHT AGING

Light aging of the lined and dammar varnished samples was undertaken at the Stichting Restauratie Atelier Limburg, Maastricht, Netherlands, using 36W Philips color 96.5 fluorescent lamps with UV filtering (transmission 15 W/lm) and an average temperature of 25°C and 60% RH. Samples were exposed for 2250.5 hours at 10,000 lux illumination, corresponding to 38.5 years equivalent museum light exposure assuming reciprocity (based on 200 lux illumination for 8 hours per day). Together with the initial aging of the samples by Nieder (2008), the samples received the equivalent of 62.5 years of museum light exposure.

COLOR MEASUREMENT

Color measurement was carried out using a Minolta Spectrophotometer CM 2600-d with a D 6500 (standard daylight) illuminant and was set to the medium aperture with the standard observation of 10°. A white standard number 7004487 was used for calibration. A template was used that facilitated repeated measurement of the same site on each sample that had been measured in the previous study (Nieder et al., 2011). The spectrophotometer was set to specular reflectance excluded (SCE_0). The average of three measurements from each site was used to calculate L*a*b* values. Reflectance measurements were taken at 10 nm intervals from 400 to 700 nm. The Commission International de L'Eclairage CIE2000 L*a*b* values were recorded, and the color difference (ΔE) was calculated: $\Delta E = \sqrt{\ *(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$.

PHOTOGRAPHY AND MICROSCOPY

Samples were photographed using a Canon SD600 SLR digital camera. Each sample was photographed before and after varnish removal in the same lighting conditions for each sample in the study using daylight and ultraviolet lamps. Samples were examined using a binocular light microscope (LM) equipped with tungsten and UV illumination at 40× to 800× magnification. Observations were recorded and compared with qualitative observations made by Nieder et al. (2011), Carlyle (2006), and Carlyle et al. (2008) of the same samples.

VARNISH SOLUBILITY

The solubility of the dammar varnish in mixtures of isooctane, propan-2-ol, and ethanol were determined. The varnish was removed from three specific locations using cotton swabs in the areas where the comparative color measurements were made, noting the solvent mixture used and the number of rolls needed to complete the varnish removal for each quadrant. Removal of varnish was intended to return the appearance of the surface of the sample as closely as possible to the untreated quadrant (in the case of the varnished quadrants) or the lined quadrant (in the case of the lined and varnished quadrants). The success of removal was determined by examining the test areas in ordinary, UV, and raking light and using LM. This strategy was chosen to replicate as closely as possible the methods used by conservators.

RESULTS AND DISCUSSION

Effects of Varnishing

Varnishing produced significant visual darkening in some samples. Selected samples with a measured visible difference of 1ΔE between varnished and unvarnished quadrants are shown in Figure 2. Darkening after varnishing was greatest in samples in glue medium, followed by emulsion; the least changed were the samples bound in oil. The change in ΔE after varnishing of the unlined glue-bound samples ranged from 4.82 to 19.02, whereas the lined samples in the same medium changed less, with ΔE ranging from 0.36 to 7.45. The glue-bound samples containing chalk absorbed the varnish and the surface remained matte. The varnished surface of the chalk in glue on jute samples had a superficial plastic appearance. The emulsion-bound samples were less darkened on varnishing (ΔE of 2.44–4.05 for unlined and 1.12–2.65 for lined samples), and the smallest color change was measured in oil-bound samples (0.32–2.48 for unlined and 0.75–1.74 for lined samples).

TABLE 1. Summary of the composition of the samples used in the study.

Binding Media	Sample Composition (size application, binding media, inorganic material, support)
Hide glue binder	gelled glue size; chalk in hide glue binder on fine-weave linen
	fluid glue size; chalk in hide glue binder on fine-weave linen
	no size, chalk in hide glue binder on fine-weave linen
	gelled glue size; chalk in hide glue binder on open-weave linen
	no size, chalk in hide glue binder on jute canvas
	gelled glue size; chalk and bone black in hide glue binder on fine-weave linen
	fluid glue size; chalk and bone black in hide glue binder on fine-weave linen
	no glue size; chalk and bone black in hide glue binder on fine-weave linen
	gelled glue size; barium sulfate in hide glue binder on jute canvas
	no size; barium sulfate in hide glue binder on jute canvas
Emulsion	gelled glue size; chalk in glue-oil emulsion binder on fine-weave linen
	fluid glue size; chalk in glue-oil emulsion binder on fine-weave linen
	no size; chalk in glue-oil emulsion binder on fine-weave linen
	gelled glue size; chalk in glue-oil emulsion binder on open-weave linen
	no size; chalk in glue-oil emulsion binder on jute canvas
	gelled glue size; barium sulfate in glue-oil emulsion binder on jute canvas
	no size; barium sulfate in glue-oil emulsion binder on jute canvas
Oil	gelled glue size; chalk in oil binder on fine-weave linen
	fluid glue size; chalk in oil binder on fine-weave linen
	no size; chalk in oil binder on fine-weave linen
	gelled glue size, double ground on open-weave linen; first ground: chalk in hide glue binder; second ground: lead white in oil binder
	gelled glue size, double ground on open-weave linen; first ground: chalk in glue-oil emulsion binder; second ground: lead white in oil binder
	gelled glue size, double ground on open-weave linen; first ground: chalk in oil binder; second ground: lead white in oil binder
	no size, double ground on open-weave linen; first ground: chalk in hide glue binder; second ground: lead white and barium sulfate in oil binder
	gelled glue size, double ground on open-weave linen; first ground: chalk in glue-oil emulsion binder; second ground: lead white and barium sulfate in oil binder
	gelled glue size; chalk in oil binder on open-weave linen
	gelled glue size, double ground on open-weave linen; first ground: chalk in oil binder; second ground: lead white and Barium sulfate in oil binder
	gelled glue size; chalk and lead white in oil binder on fine-weave linen
	fluid glue size; chalk and lead white in oil binder on fine-weave linen
	no size; chalk and lead white in oil binder on fine-weave linen
	gelled glue size; lead white in oil binder on fine- linen
	fluid glue size; lead white in oil binder on fine- linen
	no size; lead white in oil binder on fine-weave linen
	gelled glue size, triple ground on open-weave linen; first ground (applied twice): chalk and lead white in oil binder; second ground: lead white and chalk in oil binder
	gelled glue size, double ground on open-weave linen; first ground: chalk and lead white in oil binder; second ground: lead white and chalk in oil binder
	no size, double ground on open-weave linen; first ground: chalk and lead white in oil binder; second ground: lead white and chalk in oil binder
	gelled glue size; barium sulfate in oil binder on jute canvas
	no size; barium sulfate in oil binder on jute canvas
	no size; chalk in oil binder on jute canvas
	gelled glue size; lead white and barium sulfate in oil binder on open-weave linen
	fluid glue size; lead white and barium sulfate in oil binder on open-weave linen
	no size; lead white and Barium sulfate in oil binder on open-weave linen

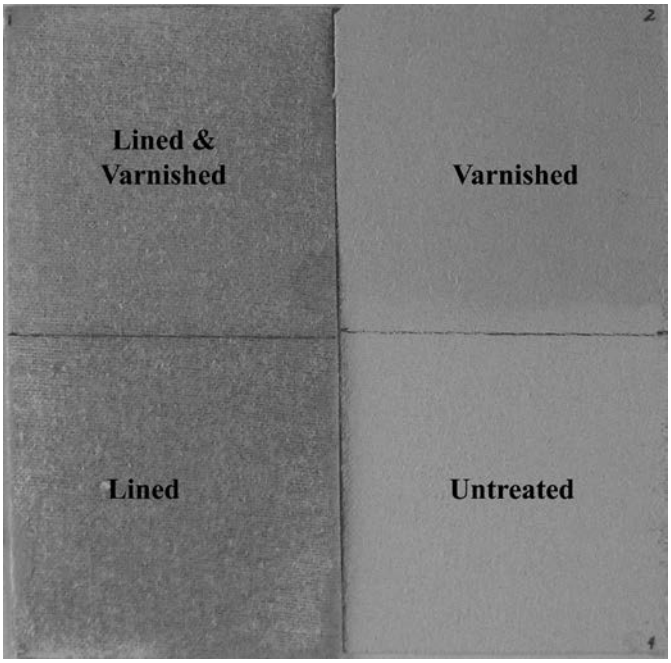


FIGURE 1. Template for sample treated and untreated quadrants. This example is composed of unsized fine-weave linen, with a single priming of chalk in hide glue.

The size layer affected the measured and observed darkening imparted by varnishing, and this was most pronounced in samples with chalk in glue binder. Grounds prepared with a cold size layer reduced absorption of the varnish into the canvas and concomitant darkening. Fluid sizing of the canvas provided some barrier to varnish absorption and darkening, whereas the unsized grounds darkened the most. A similar, though less pronounced, trend was observed and measured in samples in emulsion media. Samples containing bone black with chalk in a glue medium darkened more on varnishing than all the other samples in any medium, suggesting pigmented grounds such as those used by the Impressionists may be particularly vulnerable to darkening.

Color Change on Varnish Removal

ΔE and the percentage color change in samples after varnish removal from lined and unlined quadrants are illustrated in Figures 3 and 4. The measurable "recovery" of the unvarnished surface after varnish removal was measured by calculating the percentage change:

$$\frac{[\Delta Eu - va] - [\Delta Eu - v]}{[\Delta Eu - v]} \times 100$$

where u is the untreated quadrant, v is the varnished quadrant, and a is the area after varnish removal.

The larger the percentage change is, the more "successful" the varnish removal was in recovering the original surface. A larger percentage also reflects a significant difference in color between untreated and varnished grounds. Oil-bound samples changed the least on varnishing and lining, and thus, the small

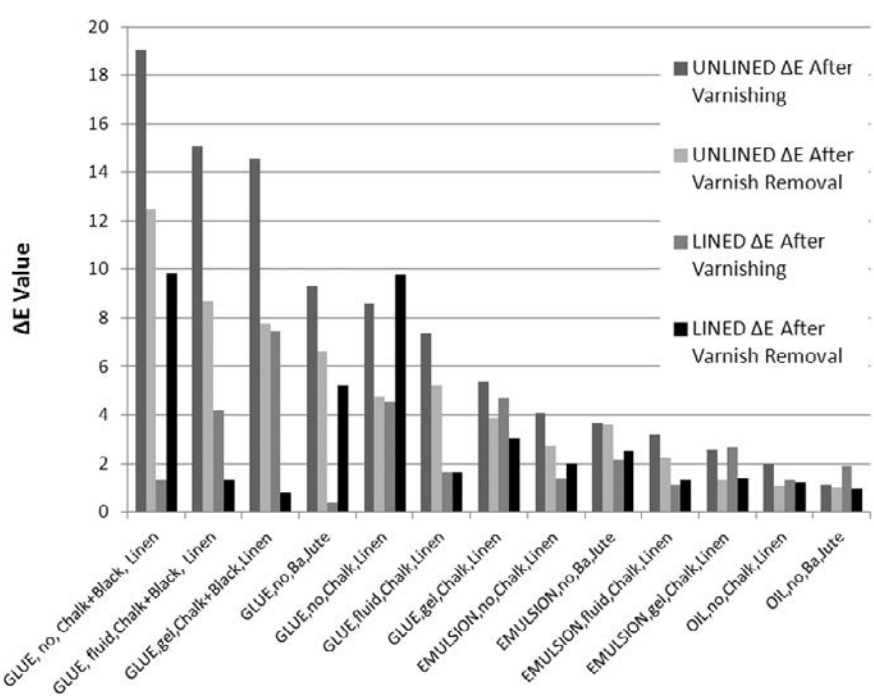


FIGURE 2. Selected ΔE values of samples after varnishing and varnish removal.

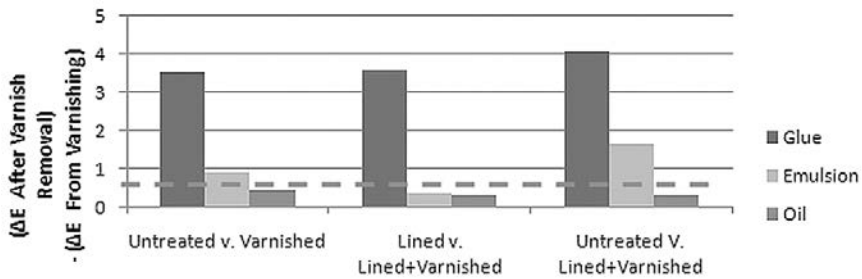


FIGURE 3. The difference in ΔE before and after varnish removal from ground samples. The dashed line at $\Delta E = 1$ indicates the threshold of visible difference.

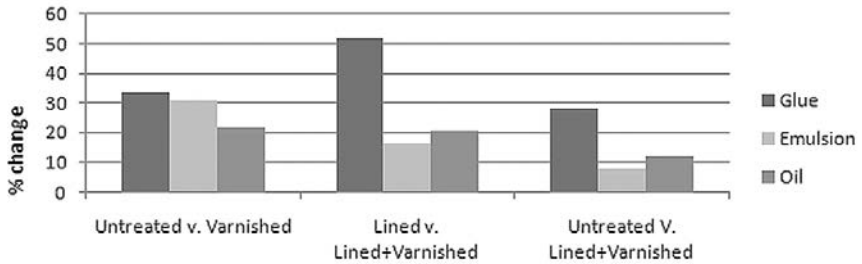


FIGURE 4. Percentage change in ΔE following varnish removal.

percentage changes represent a reversal of this shift. Although removing varnish from the lined samples was practically more straightforward, the darkening imparted by lining was greater than the recovery of the surface after varnish removal.

Glue-bound samples showed the greatest changes (on varnishing and) after varnish removal. The ΔE values after varnish removal for all the other samples (with the exception of the lined samples in emulsion medium) were below $1\Delta E$ and thus were not detectable by the eye. However, there were significant changes in these samples that are reflected in the calculated percentage change. The most successful varnish removal in terms of visible change was from glue-bound samples. The recovery of the surface was greatest in the lined samples, reflected in the percentage change. This follows practical observations that lining facilitated the removal of varnish in these samples, whereas it was more difficult to remove the varnish from the more absorbent unlined samples in glue medium. The greatest changes were measured between the untreated quadrants and the lined and varnished quadrants of the glue-bound samples. The average ΔE value of the untreated quadrant versus the lined and varnished quadrant was 14.11, reflecting the color change due to both lining and varnishing. The average ΔE value of the same quadrants following varnish removal was 10.06, demonstrating a visually significant reduction in darkening. Incomplete recovery of the unlined quadrant on varnish removal was evident from the comparison between the untreated quadrant and the varnished quadrant following varnish removal. Thus, it was not possible to recover the appearance of the unvarnished surface of the most absorbent samples, and varnishing of these samples was not reversible.

Monitoring Varnish Removal

The extent of varnish removal from oil-bound samples was most effectively monitored by change in gloss that was visible in LM and ordinary light. In UV light, samples bound in oil and emulsion media that did not contain lead white exhibited a characteristic yellow green fluorescence in the unvarnished quadrants. This cast was slightly reduced on varnishing, and when the varnish was removed using polar solvents, the fluorescent material was disturbed, and the cleaned areas appeared purple. This suggests that the solvent affected a skin of fluorescent surface material on these samples. This hypothesis was supported by the results of testing a different solvent mixture for varnish removal that did not affect the superficial fluorescent layer.

Influence of Binding Medium on Varnish Removal

The glue-bound samples required the most polar solvents and most repeated swab rolling to satisfactorily remove the varnish. Isopropanol and mixtures of iso-octane:isopropanol (3:1 or 2:1) were required, with an average of 25 swab rolls. The unlined quadrant required the same or a more polar solvent to remove the varnish compared with the lined quadrant of the same sample. In general, ΔE values decreased after varnish removal, whereas unsized samples bound in glue containing chalk, bone black, and barium sulfate measured an increase in ΔE between the lined and the lined plus varnished quadrants. This change reflects the combined effects of impregnation of the samples, the abrasion of the most raised areas of ground on peaks in the canvas weave, and varnish removal.

Removal of varnish from samples in emulsion medium required a lower-polarity solvent mixture and less mechanical action than samples in glue medium. Mixtures of iso-octane:isopropanol (4:1 and 3:1) required 20 swab rolls, and the coarse texture of the samples on jute required 40 swab rolls to remove the varnish. Varnish removal from the unlined quadrants required the same or slightly more polar solvent mixtures than the lined quadrants of the same sample. Samples containing lead white in oil were

glossy and relatively nonabsorbent and required an average of 25 rolls using a 3:1 mixture of iso-octane:isopropanol to remove the varnish from both the lined and unlined quadrants. Practically, varnish removal was most straightforward when it contained lead white as the surface was unaffected even using a solvent mixture of higher polarity. Notably, varnish from samples with multiple ground layers containing chalk and lead white mixtures was readily removable using a 4:1 mixture and 10 rolls, illustrating the influence of the underlying layers as well as the surface on varnish absorption and removal.

Influence of the Size Layer on Varnish Removability

The size layer acted as a physical barrier, preventing varnish and/or the lining adhesive penetrating the support. The gelled size was the most effective barrier, followed by fluid size, whereas varnish, adhesive, and solvents penetrated the sample most when no size was present. In removing varnish from unlined quadrants, particularly from samples bound in glue, the solvent was difficult to contain, and spreading beyond the swabbed area was visible on the reverse. This was less pronounced in samples where the canvas had a gelled size application. Varnish penetrated the structure of the unsized samples and was concomitantly more difficult to remove.

Influence of Lining on Varnish Removal

Lining adhesive provided a barrier to absorption of varnish and acted in a way similar to a gel sizing of the canvas. Varnish was easier to remove from lined samples than from the unlined quadrants because of reduced penetration of the coating. During varnish removal from wax-resin lined samples, the nonpolar component of the solvent mixture reduced the wax present on the weave tops, notably lessening the darkening effects of the lining. The influence of lining on varnish removal was most pronounced on unsized samples in glue medium. Samples in emulsion media showed a similar, though less pronounced, effect, and oil-bound samples were not affected.

Influence of the Ground's Inorganic Component on Varnish Removal

Barium sulfate in glue (and to some extent in the emulsion) media was relatively porous and absorbent, and thus, varnish removal from samples with barium sulfate in glue was more difficult. There was no significant change in color in samples containing lead white on varnishing and after varnish removal, whereas the samples containing bone black in glue medium changed the most. The reversibility of varnishing of colored grounds and paint grounds requires further study.

Influence of the Canvas Support on Varnish Removal

The rough topography of jute canvases precluded complete removal of varnish from unlined samples in all media. Otherwise, there were no significant differences between the supports with regard to varnish removal.

Practical and Aesthetic Issues for Varnish Removal from Paintings

The removal of a varnish coating from paintings of the late nineteenth and twentieth centuries that were intended to be unvarnished with view to their display might be considered part of the conservation plan for these works. The question of whether it is possible to recover the original surface of an unvarnished painting or, failing that, how to evaluate a reinterpretation of the surface requires further investigation. The present study has provided some guidelines for some of the parameters that might be considered in evaluating the success of removing a natural resin varnish from a range of ground samples similar to those used for nineteenth-century paintings and the influence of wax-resin lining on the process and results of removal. Although this study has highlighted some of the issues, the practical problems of removing varnish from paint are more complex, where selective sensitivity to solvents and cleaning reagents and mechanical methods for varnish removal are points to be taken into account. For example, conservators of paintings by Van Gogh have reported sensitivity of dark blue and green paints, medium-rich paints, and paint containing chrome and cadmium yellow pigments in his works to a range of organic solvents used for varnish removal (Van Gogh Museum, Amsterdam, unpublished treatment reports for F293; van Bommel, 2005). In addition, the physical deterioration of some red-lake-containing paints, manifest in cracking, powdering, and flaking paint, can limit complete varnish removal (Van Gogh Museum, Amsterdam, unpublished treatment report for F370). Removing varnish evenly remains a challenge, and the selection of solvent or reagent for cleaning may influence the surface quality of the underlying paint or ground (L. Mayer, Mayer & Myers Conservation, New London, Connecticut, personal communication). The pronounced texture of some Impressionist paintings requires the use of a range of cleaning tools and methods tailored for the purpose (Van Gogh Museum, Amsterdam, unpublished treatment reports; E. Hendriks and D. Ormond, Van Gogh Museum, Amsterdam, personal communication; L. van der Loeff, Kroller-Muller Museum, Otterlo, Netherlands, personal communication; I. Duvernois, Metropolitan Museum of Art, New York, personal communication).

The treatment history of an individual painting influences its current appearance and subsequent treatment. The obtained results show that wax-resin lining adhesive may reduce the porosity of some paint films, preventing the varnish from penetrating and thus facilitating its removal, supporting observations made by conservators (Duvernois, pers. comm.; E. Steele, Philips Collection, Washington, D.C., personal communicaiton; L. Hoogstrader, ICN, Rijswijk, Netherlands, personal communication). Residues from former treatments, including adhesives, consolidants, discolored retouchings, and, potentially, the nonvolatile components of cleaning reagents, further complicate treatment.

Paintings that have undergone multiple cleaning campaigns may be difficult to interpret visually as areas may be changed because of lining, paint-solvent interaction, and retouching (A. Hoenigswald, National Gallery of Art, Washington D.C., personal communication). Assessment of the surface during treatment may be informed by unvarnished examples of works by the artist; however, these paintings may have changed on aging, and the task remains interpretive. For example, Van Gogh's *Garden of the Asylum* 1889 (Figure 5) has survived unlined and unvarnished.

Technical study of the painting has characterized but not quantified material changes in the paint, and thus, the use of this work as a benchmark for the appearance of the original surface is compromised. Few artists provide written accounts of their intention for the surfaces of their works, and these also require interpretation. The expertise of visually informed conservators and evidence from technical studies provide guiding principles that lead to a practical resolution that a painting looks "right" (Hendriks, pers. comm.). In some cases the relationship between compositional elements may be difficult to read once the varnish is removed, and this has been noted in paintings that have undergone several cleaning or lining treatments (Hoenigswald, pers. comm.). To regain the spatial sense of the composition after varnish removal, selective or complete revarnishing may be undertaken. For example, after varnish removal, dark passages of paint become unsaturated and require an application of a thinly applied local varnish (such as Regalrez) by brushing, spraying,

FIGURE 5. *Garden of the Asylum* Vincent van Gogh, 1889. Oil on canvas, 72 cm × 91 cm. (Van Gogh Museum, Amsterdam; Vincent van Gogh Foundation)

or rubbing with a silk cloth (Steele, pers. comm.; Hendriks, pers. comm.; Hoenigswald, pers. comm.; P. Smithen, Tate, UK, personal communications).

As varnish affords the surface of a painting physical protection from dirt, the long-term consequences of displaying works unvarnished need serious consideration. Glazing is a practical, but not always aesthetically desirable, solution and is in keeping with Impressionist practices (thought less desirable for modern paintings). The developments in low-reflective laminated glass technology offer a feasible compromise for the display of unvarnished paintings.

CONCLUSIONS

The removal of nonoriginal varnish from paintings by Van Gogh and contemporaries who valued the matte aesthetic may be desirable as part of a conservation campaign. The results of the present study highlight the changes in the grounds due to varnish and some of the practical difficulties in recovering the original appearance of the surface after varnish removal. The implications of these findings for the appearance of the recovered unvarnished painted surface present a significant challenge for the conservator. It is clear, from both conservators' accounts and the results of the present study, that both the material composition of the work and former treatments (such as wax-resin lining) may influence the surface appearance and affect the ease of varnish removal. This study investigated the color changes imparted by varnishing and subsequent removal of varnish from prepared samples based on grounds used by Van Gogh. The results will also be relevant to the study of paintings by his contemporaries who used similar commercially prepared canvases. The problems with removing varnish from passages of paint of different composition and texture that have been noted by conservators were not investigated systematically but are clearly critical, particularly where works are to be displayed unvarnished.

Acknowledgments

This paper would not have been possible without the work done by Leslie Carlyle, Ella Hendriks, and Emily Nieder. The authors also thank Klaas Jan van den Berg, Ann Hoeningswald, Elizabeth Steele, Katja Lewerentz, Devi Ormond, Luuk van der Loeff, Lance Mayer, Isabelle Duvernois, Patricia Smithen, and Luuk Hoogsteder.

REFERENCES

Bruce-Gardner, R., G. Hedley, C. Villers.1987. *Impressionist and Post-Impressionist Masterpieces: The Courtauld Collection*. New Haven, Conn.: Yale University Press.

Callen, A. 1994. The Unvarnished Truth: Mattness, "Primitivism" and Modernity in French Painting, c.1870–1907. *The Burlington Magazine,* 136(1100):738–746.

———. 2000. *The Art of Impressionism: Painting Techniques and the Making of Modernity.* New Haven, Conn.: Yale University Press.

Carlyle, L. 2005. HART Project Report. Tate Britain, London.

———. 2006. "Historically Accurate Reconstructions of Oil Painters' Materials: An Overview of the HART Project 2002–2005." In *Reporting Highlights of the De Mayerne Programme*, ed. J. J. Boon, and E. S. B. Ferreira, pp. 63–78. The Hague: Netherlands Organization for Scientific Research.

Carlyle, L., J. J. Boon, R. Haswell, and M. Stols-Witlox. 2008. "Historically Accurate Ground Reconstructions for Oil Paintings." In *Preparation for Painting,* ed. J. Townsend, T. Doherty, G. Heydenreich, and J. Ridge, pp.110–122. London: Archetype.

Hendriks, E. 2008. Fluent Impasto in Van Gogh's Paris Paintings (1886–1888): A Strategic Effect? *Zeitschrift fur Kunsttechnologie und Konservierung,* 2:221–231.

Hendriks, E., and M. Geldof. 2007. Van Gogh's Antwerp and Paris Picture Supports (1885–1888): Reconstructing Choices. *Art Matters: Netherlands Technical Studies in Art,* 2:39–74.

Hendriks, E., and L. van Tilborgh. 2006. New Views on Van Gogh's Development in Antwerp and Paris: An Integrated Art Historical and Technical Study of his Paintings in the Van Gogh Museum. Ph.D. thesis, University of Amsterdam, Amsterdam.

Jirat-Wasiutynski, M., and H. Travers Newton Jr. 1998. "Absorbent Grounds and the Matt Aesthetic in Post Impressionist Painting." In *Painting Techniques: History, Materials and Studio Practice*, *Preprints of the Dublin IIC Congress*, ed. A. Roy and P. Smith, pp. 235–239. London: International Institute for Conservation.

Miller, D. 1983. "Conservation of Neo-Impressionist Paintings." In *The Aura of Neo-Impressionists: The W. J. Holliday Collection,* ed. E. W. Lee, and T. E. Smith, p. 29. Indianapolis, Indiana: Indianapolis Museum of Art.

Nieder, E. 2008. *The Effects of Wax-resin Lining and Varnishing on Historically Accurate Reconstructions of Van Gogh's Grounds*. Unpublished report. London: Courtauld Institute of Art, Department of Conservation and Technology.

Nieder, E., E. Hendriks, and A. Burnstock. 2011. The Effects of Wax-Resin Lining and Varnishing on Historically Accurate Reconstruction of van Gogh's Grounds. *Studies in Conservation*, 56(2):94–103.

Peres, C. 1990. "Vincent Van Gogh's Triptych of Trees in Blossom, Arles (1888) Part ii. On Egg White Varnishes." In *Cleaning, Retouching and Coatings: Technology and Practice for Easel Paintings and Polychrome Sculpture, Proceedings of the Brussels IIC Congress,* ed. J. S. Mills and P. Smith, pp. 131–133. London: International Institute for Conservation.

Schaefer, I., C. von Saint-George, and K. Lewerentz. 2009. *Painting Light: The Hidden Techniques of the Impressionists*. Milan: Skira editore.

Swicklik, M. 1993. "French Painting and the Use of Varnish, 1750–1900." In *Conservation Research*, pp. 157–174. Studies in the History of Art Monograph Series II, No. 41. Washington, D.C.: National Gallery of Art.

van Bommel, M., M. Geldof, and E. Hendriks. 2005. An Investigation of Organic Red Pigments Used in Paintings by Vincent van Gogh. *Art Matters*: *Netherlands Technical Studies in Art*, 3:129–153.

Extended Abstract—Oxalate-Rich Surface Layers on Paintings: Implications for Interpretation and Cleaning

Ken Sutherland, Beth Price, Andrew Lins, and Irma Passeri

Although oxalate salts have been the subject of extensive research as alteration products on calcareous substrates (e.g. stone and fresco), there has been relatively little discussion of their occurrence on other objects, such as easel paintings. An understanding of these materials is important since they can be responsible for significant changes in the surface appearance of artworks and the solubility of the matrices in which the oxalates are formed. The altered, oxalate-rich surface layers can present substantial challenges for the visual interpretation of the painted surfaces, the accurate scientific characterization of the original materials, and the development of appropriate and effective cleaning methods.

Oxalate-containing layers or deposits have been reported on a variety of noncalcareous substrates, including glass (Drewello and Weissmann, 1997; Messal et al., 1999), bronze (Alunno-Rossetti and Marabelli, 1976; Nassau et al., 1987; Mazzeo et al., 1989; Olmi et al., 1991; Matteini et al., 1991; Selwyn et al., 1996), human remains (mummy skin; Cotte et al., 2005), and polychrome wood (Arbizzani and Casellato, 2002) and easel paintings (Salvadó et al., 2002; Bracco and Ciappi, 2002:329; Matteini et al., 2002:396–397; Sutherland et al., 2005; Spring et al., 2005; Higgitt and White, 2005; Sutherland et al., 2006; van Loon, 2008:184–186). The oxalate salts of calcium, whewellite (calcium oxalate monohydrate) and weddellite (calcium oxalate dihydrate), are those most commonly encountered on painted surfaces, although copper oxalates have also been identified in paint layers containing copper pigments (Higgitt and White, 2005:93; Castro et al., 2008). In most cases these compounds are found in deteriorated organic surface layers.

Samples from a number of paintings in the collection of the Philadelphia Museum of Art, including three Italian paintings on wood panel dating from the fourteenth and sixteenth centuries, were characterized using Fourier transform infrared microspectroscopy, X-ray diffraction, gas chromatography mass spectrometry, and scanning electron microscopy with energy dispersive spectroscopy. The surface layers studied were remnants of what appeared to be colored glazes in the case of two paintings by Pontormo (circa 1494–1556/1557) and Jacopino del Conte (1510–1598) and an early varnish on a painting by Ugolino de Nerio (fourteenth century). Among the components detected in all three cases were significant levels of calcium oxalates.

A degraded brown layer on Pontormo's *Portrait of Alessandro de' Medici* (1534–1535; see Figure 1) was studied in detail, and results from the analysis of cross-section and scraping samples suggested that it consisted of remnants of an early or original pigmented glaze layer in which particulate surface dirt had become embedded. Fourier transform

***Ken Sutherland, Beth Price,** and **Andrew Lins**, Conservation Department, Philadelphia Museum of Art, Box 7646, Philadelphia, Pennsylvania 19101-7646, USA. **Irma Passeri**, Conservation Department, Yale University Art Gallery, Box 208271, New Haven, Connecticut 06520-8271, USA. Correspondence: ksutherland@philamuseum.org.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

FIGURE 1. Pontormo (Jacopo Carucci), *Alessandro de' Medici*, 1534–1535. Oil on panel, 101 × 82 cm. Courtesy of Philadelphia Museum of Art, John G. Johnson Collection, catalog 83.

infrared microspectroscopy analysis indicated the presence of calcium oxalate dihydrate in the layer. Oxalate was also detected by gas chromatography mass spectrometry (as its *tert*-butyldimethylsilyl derivative), and its mineral form was confirmed by X-ray diffraction (Figure 2). Although the glaze layer was disfigured, having become darkened and opaque as a result of its physical and chemical alteration, it was left intact during a cleaning treatment carried out in 2001–2003. The study of the glaze and other materials of this painting are discussed in previous publications (Tucker et al., 2004; Sutherland et al., 2005).

Various mechanisms (biological and chemical) have been proposed for the formation of oxalate films on artworks (Matteini and Moles, 1986). In the cases studied at the Philadelphia Museum of Art , the oxalate minerals likely derive from the gradual oxidative degradation of organic materials in the surface layers and their reaction with calcium-containing pigments and/or particulate dirt. The resistance of the calcium oxalates to organic solvents and other cleaning agents presumably contributes to their enrichment on the surface. Generally speaking, the alteration (mineralization) of organic surface layers on paintings may present significant practical and, in the case of early or original materials such as varnishes and glazes, ethical challenges in the development of cleaning strategies. The use of the term "oxalate patina," common in relation to stone and monuments but occasionally encountered in reference to paintings (Colombini et al., 2000), implies some ambiguity in whether or not such layers may be considered visually acceptable. As with discussions of other types of alteration, particularly the discoloration of varnishes, this is a complex issue that will relate to the extent of material and visual change, as well as to differences in cleaning ideology. Further research is needed to understand more fully the factors

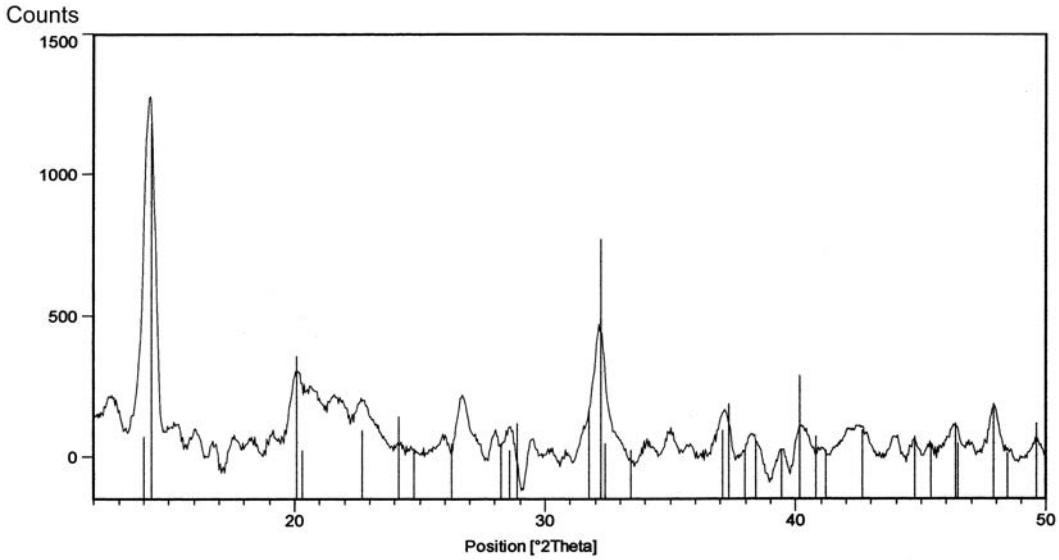


FIGURE 2. X-ray diffraction pattern of sample from brown surface layer in green-painted area of background, overlaid with reference pattern for weddellite (indicated by vertical lines; reference pattern: Joint Committee on Powder Diffraction Standards 17-541).

influencing the development of oxalate layers on paintings and their visual impact and, where necessary, to inform safe and effective methods for their removal.

REFERENCES

Alunno-Rossetti, V., and M. Marabelli. 1976. Analyses of the Patinas of a Gilded Horse of St Mark's Basilica in Venice: Corrosion Mechanisms and Conservation Problems. *Studies in Conservation*, 21:161–170. http://dx.doi.org/10.2307/1505640.

Arbizzani, R., and U. Casellato. 2002. "The Scrovegni Chapel at Padova: Chemical Investigations on the Polychromy of Wooden Furnishings." In *The Fifth International Infrared and Raman Users Group Conference (IRUG5), Conference Program and Abstracts*, pp. 117–119. Los Angeles: Getty Conservation Institute.

Bracco, P., and O. Ciappi. 2002. "Technique of Execution, State of Conservation and Restoration of the Crucifix in Relation to Other Works by Giotto. The Painted Surface." In *Giotto: The Santa Maria Novella Crucifix*, English ed., ed. M. Ciatti and M. Seidel, pp. 273–359. Florence: EDIFIR–Edizioni Firenze.

Castro, K., A. Sarmiento, I. Martínez-Arkarazo, J. M. Madariaga, and L. A. Fernández. 2008. Green Copper Pigments Biodegradation in Cultural Heritage: From Malachite to Moolooite, Thermodynamic Modeling, X-ray Fluorescence, and Raman Evidence. *Analytical Chemistry*, 80:4103–4110. http://dx.doi.org/10.1021/ac800255w.

Colombini, M. P., F. Modugno, E. Menicagli, R. Fuoco, and A. Giacomelli. 2000. GC-MS Characterization of Proteinaceous and Lipid Binders in UV Aged Polychrome Artifacts. *Microchemical Journal*, 67:291–300. http://dx.doi.org/10.1016/S0026-265X(00)00075-8.

Cotte, M., P. Walter, G. Tsoucaris, and P. Dumas. 2005. Studying Skin of an Egyptian Mummy by Infrared Microscopy. *Vibrational Spectroscopy*, 38:159–167. http://dx.doi.org/10.1016/j.vibspec.2005.02.024.

Drewello, R., and R. Weissmann. 1997. Microbially Influenced Corrosion of Glass. *Applied Microbiology and Biotechnology*, 47:337–346. http://dx.doi.org/10.1007/s002530050937.

Higgitt, C., and R. White. 2005. Analyses of Paint Media: New Studies of Italian Paintings of the Fifteenth and Sixteenth Centuries. *National Gallery Technical Bulletin*, 26:88–104.

Matteini, M., and A. Moles. 1986. Le Patine di Ossalato di Calcio sui Manufatti in Marmo. [Calcium Oxalate Patinas on Marble Objects.] *OPD Restauro: Quaderni dell'Opificio delle Pietre Dure e Laboratori di Restauro di Firenze,* Numero Speciale:65–73.

Matteini, M., A. Moles, G. Lanterna, C. Lalli, M. R. Nepoti, M. Rizzi, and I. Tosini. 2002. "Characteristics of the Materials and Techniques." In *Giotto: The Santa Maria Novella Crucifix*, English ed., ed. M. Ciatti and M. Seidel, pp. 387–403. Florence: EDIFIR–Edizioni Firenze

Matteini, M., A. Moles, and M. R. Nepoti. 1991. Caratterizzazione dei Prodotti di Alterazione di Superficie Mediante Spettrofotometria IR. [Characterization of Surface Alteration Products Using IR Spectrophotometry.] *OPD Restauro: Quaderni dell'Opificio delle Pietre Dure e Laboratori di Restauro di Firenze*, 3:36–39.

Mazzeo, R., G. Chiavari, and G. Morigi. 1989. "Identificazione ed origine di patine ad ossalato su monumenti bronzei: Il caso del portale centrale del Duomo di Loreto (AN). [Identification and Origin of Oxalate Patinas on Bronze Monuments: The Main Door of Loreto Church in Ancona.]" In *Le pellicole ad ossalati: Origine e significato nella conservazione delle opere d'arte* [Oxalate Films: Origin and Significance in the Conservation of Works of Art], ed. G. Alessandrini, pp. 271–279. Milan: Gino Bozza.

Messal, C., T. Gerber, and G. Ballin. 1999. Biodeterioration an Oxidischen Gläsern. Teil II: Biokorrosive Ursachen der Glaspestbildung an Mecklenburger Waldgläsern. [Biodeterioration on Oxide Glasses. Part II: Biocorrosive Reasons for Appearance of Glaspest of Antique Glasses like Mecklenburger Waldglas.] *Materials and Corrosion*, 50:166–172. http://dx.doi.org/10.1002/(SICI)1521-4176(199903)50:3<166::AID-MACO166>3.0.CO;2-8.

Nassau, K., P. K. Gallagher, A. E. Miller, and T. E. Graedel. 1987. The Characterization of Patina Components by X-ray Diffraction and Evolved Gas Analysis. *Corrosion Science*, 27:669–684. http://dx.doi.org/10.1016/0010-938X(87)90049-7.

Olmi, F., C. Sabelli, and R. Trosti-Ferroni. 1991. Indagini mineralogiche sulle patine di alterazione. [Mineralogical Investigations of Alteration Patinas.] *OPD Restauro: Quaderni dell'Opificio delle Pietre Dure e Laboratori di Restauro di Firenze* , 3:32–35.

Salvadó, N., T. Pradell, E. Pantos, M. Z. Papiz, J. Molera, M. Seco, and M. Vendrell-Saz. 2002. Identification of Copper-based Green Pigments in Jaume Huguet's Gothic Altarpieces by Fourier Transform Infrared Microspectroscopy and Synchrotron Radiation X-ray Diffraction. *Journal of Synchrotron Radiation*, 9:215–222. http://dx.doi.org/10.1107/S0909049502007859.

Selwyn, L. S., N. E. Binnie, J. Poitras, M. E. Laver, and D. A. Downham. 1996. Outdoor Bronze Statues: Analysis of Metal and Surface Samples. *Studies in Conservation*, 41:205–228. http://dx.doi.org/10.2307/1506541.

Spring, M., C. Higgitt, and D. Saunders. 2005. Investigation of Pigment-Medium Interaction Processes in Oil Paint Containing Degraded Smalt. *National Gallery Technical Bulletin*, 26:56–69.

Sutherland, K., B. Price, I. Passeri, and M. Tucker. 2005. A Study of the Materials of Pontormo's "Portrait of Alessandro de' Medici." In *Materials Issues in Art and Archaeology VII;* MRS 852, ed. P. B, Vandiver, J. L. Mass, And A. Murray, pp. 141–152. Warrendale, Pa: Materials Research Society.

Sutherland, K., B. Price, and A. Lins. 2006. "The Characterization of Degraded, Oxalate-Rich Surface Layers on Paintings." In *The Seventh Biennial Gathering of the Infrared and Raman Users Group (IRUG7), Abstracts and Executive Summaries of Contributions*, pp. 41–42. New York: Museum of Modern Art.

Tucker, M., I. Passeri, K. Sutherland, and B. Price. 2004. "Technique and Pontormo's Portrait of Alessandro de' Medici." In *Pontormo, Bronzino, and the Medici: The Transformation of the Renaissance Portrait in Florence*, ed. C. Strehlke, pp. 34–54. Philadelphia: Philadelphia Museum of Art.

van Loon, A. 2008. Color Changes and Chemical Reactivity in Seventeenth-Century Oil Paintings. Ph.D. thesis, University of Amsterdam, Amsterdam.

Characterization and Stability Issues of Artists' Alkyd Paints

Rebecca Ploeger and Oscar Chiantore

ABSTRACT. Alkyd paints were developed mainly for industrial and household applications and have received minor attention in the art conservation field. The conservation literature is still sparse on the chemistry, characterization, and stability of these materials and even more so on cleaning procedures and conservation recommendations. This does not mean that artists have not used them; rather, they have been (and still are) using them widely. The aims of this paper are to provide a general introduction to these paints and information on how they can be efficiently characterized in works of art, to discuss some of their stability issues, and to give simple recommendations for their conservation. Through a number of analytical techniques the characterization of artists' alkyds and their drying, aging, and degradation processes are explored. On the basis of the information gained and from practical suggestions of conservators, basic guidelines are suggested with the hope that these can be tested and confirmed in the field.

INTRODUCTION

One of the most important classes of binding media of the twentieth century is represented by the alkyd resins. The first alkyds were known as "glyptals" and appeared in the early 1900s. The term alkyd is derived from the polyalcohol and diacid monomers used to make the polyester polymer; the first oil-modified alkyd resins, what we generally refer to as an alkyd today, appeared in the 1920s. However, it was only after the World War II that research and development of alkyds really took off.

Alkyd resins are made by condensation polymerization of polyols, diacids, and siccative oils or free fatty acids, and the final resin is composed of a polyester backbone, which on its own is a brittle, highly branched polymer, and dangling fatty acids, which serve to reduce the amount of cross-linking, creating a more flexible polymer. The polymer is dissolved and carried in a solvent which varies on the basis of the amount of fatty acids present. In the case of alkyd resins for artists' alkyd paints, the resins can be carried in a nonpolar aliphatic hydrocarbon solvent (i.e., mineral spirits).

The main advantage and selling point of artists' alkyds is their rapid drying (18–24 hours, touch dry), regardless of the color (Staples, 1982a), which allows artists to create works swiftly while maintaining some of the aesthetics and working properties of a traditional oil paint (Staples, 1982a, 1982b). The fast drying also makes them ideal for underpainting, impasto, layers, and glazing. The general paint rules that apply to oils also can be applied to alkyds; similar painting grounds can be used, as well as varnishes, brushes, painting knives, and solvents used for cleaning. Artists' alkyds are completely

***Rebecca Ploeger** and **Oscar Chiantore**, Department of Chemistry, University of Torino, Via Pietro Giuria 7, 10125 Torino, Italy. Correspondence: Oscar Chiantore, oscar.chiantore@unito.it.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

intermixable with traditional oil paints, and intermediate drying rates can be found by their mixing, so mixed-media paintings can be created without problems (Staples, 1982a). Also, alkyd paints remain soluble in turpentine and white spirits for the duration of a typically working session (6–8 hours); therefore, the initial stiffening can be reversed, and an artist can control the semidry state for long periods of time and make simple modifications. Diluting these paints in solvents can allow an artist to achieve a watercolor painting effect without significant bleeding of the colors into each other (Staples, 1982a).

The type of alkyd resin used in artists' alkyd paints is a long-oil alkyd, which is an oil-modified polyester polymer that contains between 56–70 weight percent (wt %) fatty acids. The oil length is the weight percent of fatty acids in the finished resin. Alkyd resins, based on specific applications, are grouped between short oil (35–45 wt %), medium oil (46–55 wt %), long oil (56–70 wt %), and very long oil (above 70 wt %). Changing the oil length and oil type has a great impact on the properties and ultimate applications of the resins; however, many of them are out of the scope for this work, and therefore, only long-oil alkyds will be discussed.

The rapid touch drying of artists' alkyds is due to solvent evaporation (physical drying) and the high molecular weight of the resin, which requires fewer cross-links to form a coherent film. The unsaturation of the fatty acids is, for the most part, unaffected during the manufacturing of the resin, so the chemical drying properties of the alkyd paints are similar to those of traditional oil paints; the cross-linking and film formation takes place by autoxidation, aided by catalysts, such as Co, Zr, and Ca. However, the higher molecular weight of alkyd resins has a disadvantage since alkyds become harder and therefore more brittle at an earlier stage of their aging process than oil colors do (Lack, 1988). Also, long-oil alkyd resins tend to yellow upon aging, especially with linseed oil-based resins that have a high unsaturated fatty acid content. To overcome this, semidrying oils, such as soya, safflower, etc., can be used to manufacture alkyds. The small decrease in drying efficiency is countered by the fact that semidrying oils have a lower tendency to discolor during aging. Figure 1 summarizes alkyd properties obtained with different oils.

As mentioned above, long-oil alkyd film formation occurs by catalyzed autoxidation. During this process, hydroperoxides are formed and degrade into radical species that participate in cross-linking by recombination reactions resulting in ether, peroxy, and carbon-carbon cross-links (Muizebelt et al., 1994; Mallégol et al., 2000). If cross-linking proceeds to an excessive degree, β-scission can occur, forming lower molecular weight degradation products as well as a number of other oxygenated degradation species, such as carboxylic acids, aldehydes, and alcohols. The oxygenated species can change forces within the film and, to a small degree, the film surface interactions with different solvents (Ploeger et al., 2009a). The lower molecular weight species can be lost through evaporation and extraction, contributing

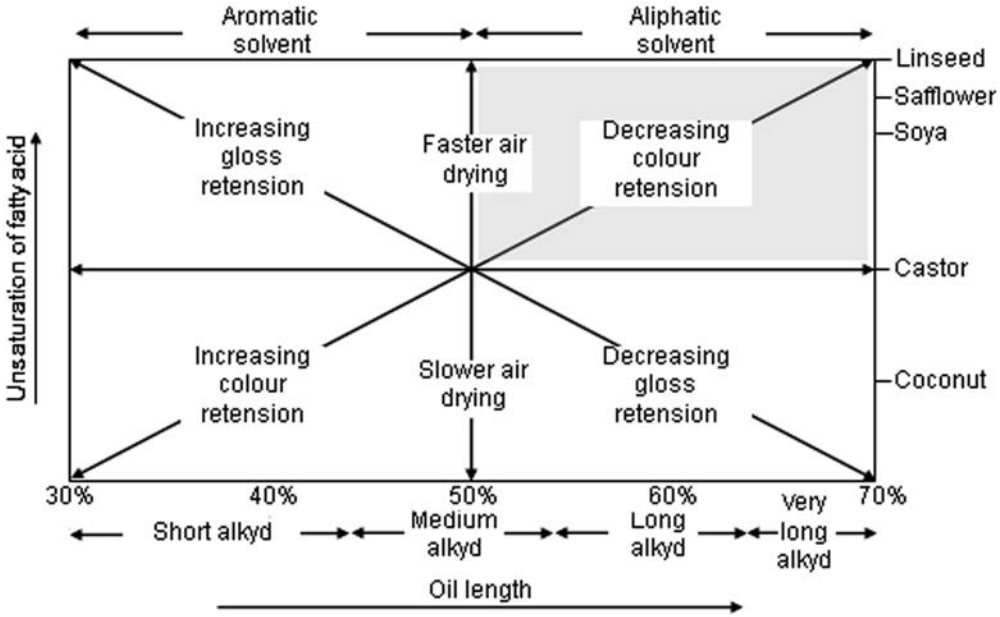


FIGURE 1. Summary of alkyd properties obtained by varying the oil type and oil length of the resin. The shaded top right section represents the area of artists' alkyd resins. Alkyds in the left half are generally for spray and industrial use with lacquer-type drying and curing. Alkyds in the right half are more for brushing applications and have been modified for flowability and better stability in containers. Modified after Patton (1962).

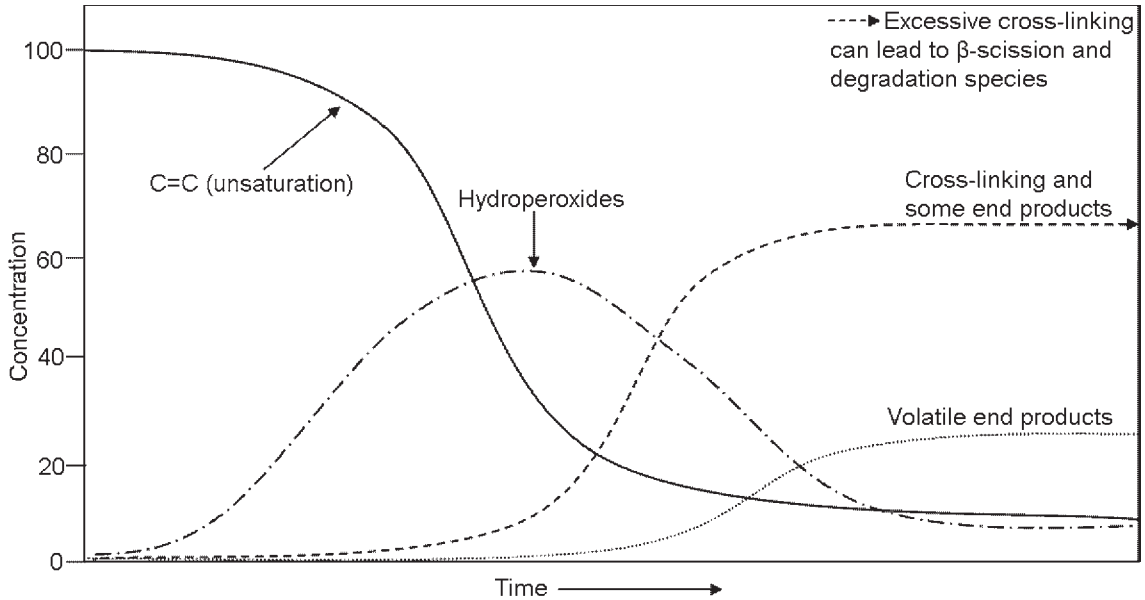


FIGURE 2. Film formation and degradation processes. Modified after van Gorkum and Bouwman (2005).

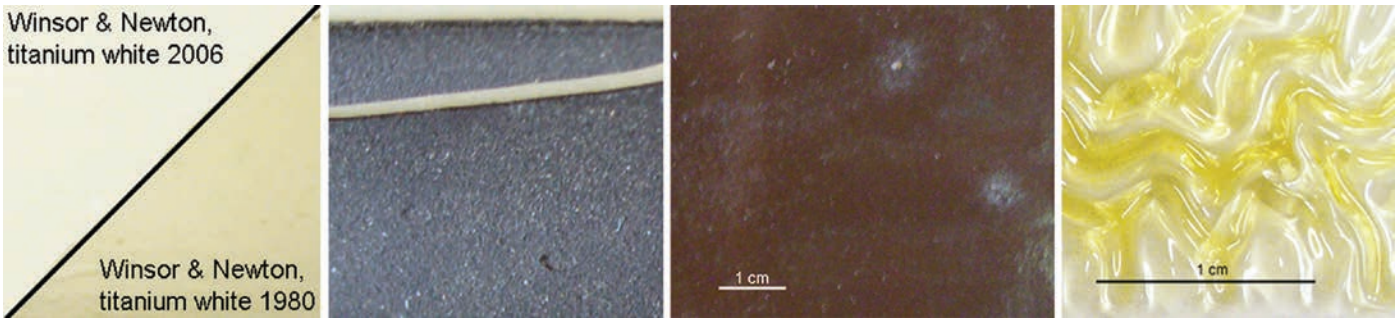


FIGURE 3. Conservation problems encountered with alkyd paints and resins. From left to right: yellowing with age, brittleness (cracking), blooming effect, and wrinkling during drying.

to an increased brittleness of the film since these species could otherwise act as plasticizing agents. Figure 2 describes the general film formation and degradation processes.

Conservation problems encountered with alkyd paints are few but significant in their impact on the stability and appearance of the work of art (Figure 3). The main concerns are (1) pigment-dependent wrinkling and aging of the films, (2) relative humidity and temperature-dependent migration of fatty acids, and possibly other additives, resulting in a "blooming" effect, (3) significant stiffening and cracking of the films with age, and (4) rapid yellowing and darkening.

This paper addresses some of the characterization and stability issues encountered with artists' alkyd paints, which can be comparable to industrial unmodified alkyd formulations. Some practical conservation issues and solutions will be discussed, and basic storage guidelines will be proposed. The results from the artists' alkyd paints are based on studies of Winsor & Newton Artists' Alkyd Colours (discontinued), London Alkyd Colours (discontinued), Griffin Alkyds (currently available) and reference materials, Ferrario Alkyd (Colore Alchidico), Da Vinci Paint Co. Leonardo Oil with Alkyd (formulation from 2006), Paints Dry Quick (PDQ) Quick Dry Oil (discontinued), and various alkyd media.

DISCUSSION

Characterization

In order to identify the presence of an alkyd resin, a number of analytical techniques can be used. One of the most common is

Fourier transform infrared spectroscopy attenuated total reflectance (FTIR-ATR). A long-oil alkyd resin can be identified by its characteristic FTIR-ATR spectrum, containing a broad hydroxyl group peak at 3440cm^{-1} (broad rounded peak), (C-H)CH_2 asymmetric and symmetric stretching and bending peaks at 2,925, 2,855, and 1,465 cm^{-1} respectively, and a strong C=O stretching peak around 1,726 cm^{-1} and C-O and fingerprint peaks at 1,256 cm^{-1} (strong, likely due to esters) and 1,120 cm^{-1}.

The aromatic rings in the polyester backbone can be identified by the sharp doublet aromatic stretching peaks at 1,600 and 1,580 cm^{-1}, the strong unsaturated ring in-plane deformation peak at 1,071 cm^{-1}, and the out-of-plane deformation peaks at 741 and 705 cm^{-1}. Pigments, extenders or fillers, and other additives can complicate spectral interpretation and must be taken into consideration. A typical long-alkyd resin FTIR-ATR spectrum can be found in Figure 4 (for experimental details, see Ploeger, 2008).

In order to disclose the monomers used to manufacture an alkyd resin, pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS) or thermally assisted hydrolysis and methylation (THM)-GC-MS can be applied. Alkyd resins undergo thermal fragmentation, and the resulting monomers, such as phthalic acid (diacid), pentaerythritol (polyol), and individual fatty acids, can be identified. To observe all the components, it is recommended to derivatize the sample since some of the more polar molecules may not elute during the analysis (Ploeger, 2008). Using Py-GC-MS, it was found that the resins containing isophthalic acid (*m*-phthalic acid) as the major diacid in the polyester backbone, such as in the Ferrario, Da Vinci Paint Co., and several PDQ paints, could be confused with other binders since they did not produce a characteristic peak as does phthalic acid (*o*-phthalic acid, which elutes as phthalic anhydride), the principal diacid in the Winsor & Newton paints. Online derivatization using tetramethylammonium hydroxide (TMAH) allowed detection and identification of isophthalic acid, as well as all the fatty acids, the polyol (pentaerythritol), and glycerol (if present). The THM-GC-MS pyrograms for these two types of typical long-oil alkyd paint formulations can be found in Figure 4 (for experimental details, see Ploeger, 2008). Additives can also be detected; for example, Figure 4 shows that the Ferrario Alkyd paint contains a phthalate-based plasticizer (peak 10) and that the Winsor & Newton Griffin titanium white contains a hydrogenated castor oil (peaks 11 and 12), likely as a stabilizer or a rheology modifier. A small amount of wax was also found in the Da Vinci Paint Co. paints, and it has been shown that the Winsor & Newton Griffin paints also contain a wax, as well as possibly a small amount of plasticizer, which could be identified only after extraction experiments (Fuesers, 2006).

Stability

The most obvious stability issue concerning alkyds paints is their relatively rapid stiffening during aging. This is due to the resin having a high molecular weight and a bulky polymer backbone, so fewer cross-links are required before a coherent film is formed. As chemical drying and film formation progresses, the flexibility of the film decreases. If oxidation reactions continue after film formation has finished, it can lead to the deterioration of the film and its properties. These processes can be excessive cross-linking, chain scission, and the loss of volatile products

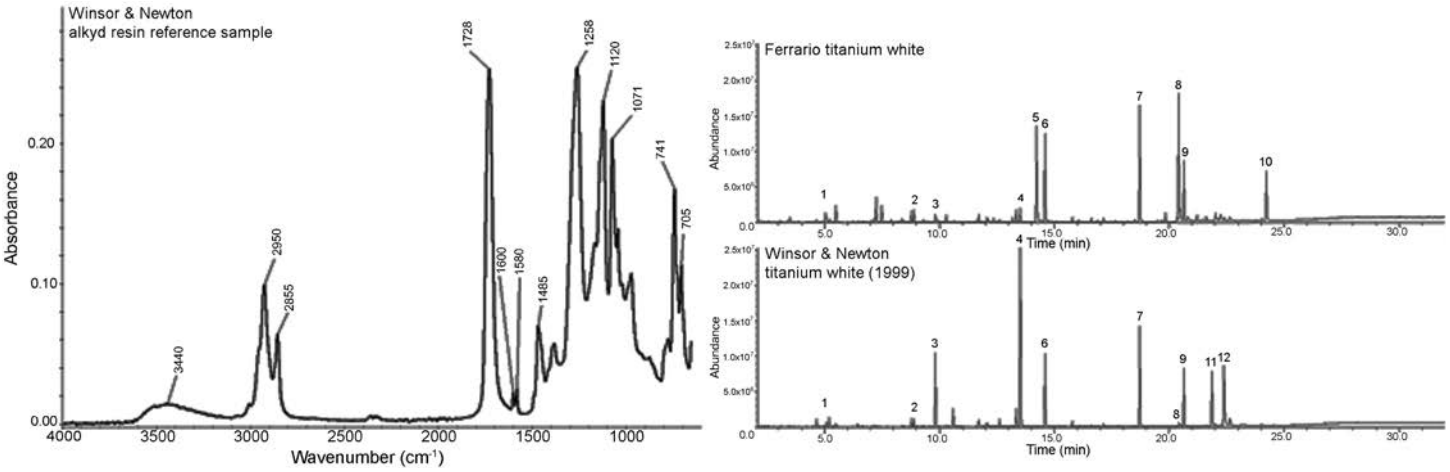


FIGURE 4. (left) The FTIR-ATR spectrum of an alkyd resin reference sample (Winsor & Newton). (top right) THM-GC/MS pyrogram of Ferrario titanium white. (bottom right) THM-GC/MS pyrogram of Winsor & Newton (Griffin) titanium white (cast in 1999). The numbered peaks (all derivatized) refer to (1) a group of glycerol fragments (around retention time T_r = 5 min), (2) fully methylated pentaerythritol (T_r = 8.9 min), (3) tri-methylated pentaerythritol (T_r = 9.8 min), (4) phthalic acid (T_r = 13.5 min), (5) isophthalic acid (T_r = 14.2 min), (6) azelaic acid (T_r = 14.6 min), (7) palmitic acid (T_r = 18.7 min), (8) oleic acid (T_r = 20.4 min), (9) stearic acid (T_r = 20.7 min), (10) phthalate plasticizer (T_r = 24.3 min), (11) 12-methoxystearic acid (T_r = 21.9 min), and (12) 12-hydroxystearic acid (T_r = 22.4 min). Benzoic acid is also present at a low amount around T_r = 8.4 min.

(Saunders, 1973). These problems can be compared to those of traditional oil paints, which indicate that it is the fatty acid portion of the alkyd that gives rise to many of these issues. If cross-linking continues to an excessive degree, the stiffening of the polymer chains will start to hinder further cross-linking reactions, and the competitive degradation of β-scission will become prevalent. The β-scission results in the formation of a low molecular weight species and radical species. The low molecular weight molecules can remain in the film or be lost by volatilization (Lazzari and Chiantore, 1999) or through solvent treatments. Alkyds are also susceptible to hydrolysis at the fatty acid ester linkages, but not with the same effects or rate as oil paints (O'Neill, 1970). Unfortunately, there is limited information in the literature about the hydrolysis of alkyd paints. The identification (Sonoda, 1998; Schilling et al., 2004; Fuesers, 2006; Ploeger et al., 2008) and extraction (Fuesers, 2006) of azelaic acid in aged films (even after limited aging) indicates that there is some degree of hydrolysis. Free azelaic acid is formed by two separate reaction steps: (1) the oxidation at the C9 position of the unsaturated fatty acid and (2) the hydrolysis of the ester bond (Erhardt et al., 2005).

These processes and their consequences were examined by a number of techniques. The first was an optical contact angle technique that examines the contact angle of a small drop of liquid on the surface of a material (for experimental details, see Ploeger et al., 2009a). The results from these experiments provide information on the polarity and free surface energy of the surface. As an example, if a surface is very hydrophobic (nonpolar), water will bead and not wet the surface; however, if the surface is very hydrophilic (with polar groups), it will spread and wet the surface. In the case of alkyds, the formation of oxidative species during accelerated photoaging was monitored with the assumption that an increase in oxygenated species would increase the polarity of the surface and subsequently change the contact angle of the solvents on the surfaces of the paint films. The results provided insight into the rates of oxygen uptake and oxidative degradation along the film surfaces. This can also be confirmed by following the broadening of the carbonyl peak using FTIR-ATR. The raw alkyd resin showed a linear decrease in the distilled water contact angle, indicating an increase in polarity, after approximately 500 hours of accelerated aging, whereas the alkyd paints showed a plateau between 500 and 1500 hours before starting to decrease. It is assumed that the plateau is an induction period caused by UV stabilizers present in the paint formulations.

In the first 150 hours of accelerated aging, the rapid changes in contact angles are attributed to oxygen uptake into the films. The concentration of hydroperoxy groups involved in autoxidation increases, peaking between 25 and 100 hours depending on formulations, since high amounts of atmospheric oxygen can be absorbed into oil paint films in the first days of drying. After this point, the hydroperoxy groups are consumed as cross-linking and film formation progresses. This phenomenon can be observed with differential scanning calorimetry (DSC), which measures the heat transfer in and out of an entire sample (surface and bulk) over a temperature range (for experimental details, see Ploeger et al., 2009b). For alkyds, the hydroperoxy group decomposition and subsequent recombination reactions are highly exothermic, and this results in an exothermic peak between 100° and 200°C in the DSC pattern. The higher the concentration of hydroperoxy groups is, the greater the peak area is. After approximately 1,000 hours of aging, there is a relatively constant low hydroperoxy group concentration. This is the result of the end of cross-linking, and the small amount of hydroperoxy groups left represents the steady concentration of these groups during the degradation processes. The results for the accelerated photoaging of the Winsor & Newton raw alkyd resin reference are shown in Figure 5. It can be seen that with aging, the surface contact angle decreases, oxygenated species along the surface are formed (FTIR-ATR carbonyl

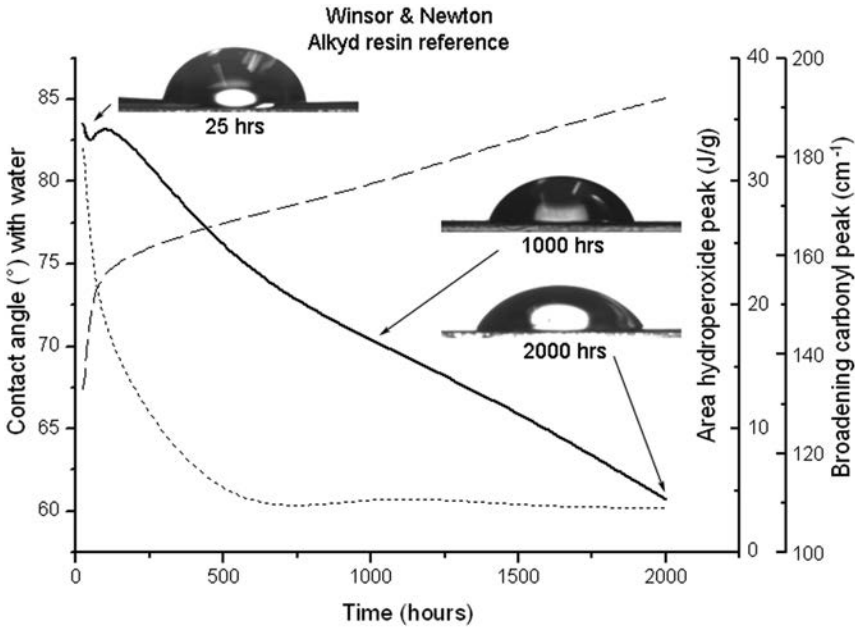


FIGURE 5. Rates of hydroperoxide consumption using DSC (dotted line), decrease in contact angle (solid line), and carbonyl peak broadening using FTIR-ATR (dashed line). The hydroperoxide concentration represents cross-linking, the decrease in contact angle indicates an increase in polarity of the surface of the film, and the broadening of the carbonyl peak indicates the formation of oxygenated species.

peak broadening), and the majority of the bulk cross-linking occurs in about 500 hours (DSC hydroperoxide peak area).

The films become stiff upon aging, and some can be extremely fragile. An increase in film density was observed with thermogravimetric analysis by a small shift in the thermal stability curves to higher temperatures (for experimental details, see Ploeger et al., 2009b). Thermogravimetric analysis provides information about the thermal stability and degradation of a material over a temperature range. A shift in the initial decomposition of the curves represents a difference, in this case an increase, in the thermal stability of the films with age. The stiffening was also observed by changes in the glass transition temperature T_g using DSC. Artists' alkyd paints that were naturally aged 1, 8, and 27 years (at the time of analysis) showed an increase in T_g with age. The samples cast in 1980 had T_g at or above room temperature, which means that with age these films can be brittle at ambient temperatures. The differences in T_g of the aged alkyds also suggest a long-term pigment dependence on the aging behaviors of these paints; for example, the Winsor & Newton Artists' Alkyd burnt umber paint from 1980 had a T_g of 41°C, whereas the titanium white temperature was around 29°C. The burnt umber pigment likely contains manganese, which will enhance the drying of the alkyd. These phenomena can be correlated back to the excessive cross-linking and subsequent degradation reactions and their consequences. Despite the uptake of oxygen the mass of the organic component of oil paints diminishes during aging, through the loss of volatile scission products (O'Neill, 1970; Lazzari and Chiantore, 1999). The formation of low molecular weight molecules in alkyd media has been demonstrated by O'Neill (1970) and Muizebelt et al. (1994).

PRACTICAL EXAMPLES

To help fill the gap in the literature concerning the cleaning of alkyd paintings, two practical examples will be presented. The first is the painting *Spatial Concept* by Lucio Fontana created in 1953. This painting has a dark blue glossy alkyd background with holes and glass fragments glued on with a polyvinyl acetate adhesive on a prepared canvas. The alkyd paint, likely an outdoor alkyd house paint, was extremely brittle, and if the canvas support were stressed, the paint layer would crack easily. It was also attracting dust and particulate matter to the surface electrostatically. During the testing of cleaning solvents, it was noted that the painting was extremely sensitive to many traditional nonpolar hydrocarbon and polar solvents used for cleaning; an immediate blooming effect was observed, with an opaque mark left after drying. The blooming effect could be due to solvent penetration and some swelling and/or leaching of additives or low molecular weight molecules from the film. For many solvents, maximum swelling in alkyds is reached within 2 minutes, except for water, which shows a slower swelling rate (Fuesers and Zumbühl, 2008). Cleaning was performed first with a preliminary dry cleaning using Wishab powder removed by a conservation vacuum cleaner, followed by a wet cleaning with a chelating solution (1% sodium citrate aqueous solution) buffered to pH 6.5 to prevent any interference with paint layer. The solution was placed on the paint surface and immediately removed with a surgical micropump without any mechanical action. Finally, the surface was rinsed with deionized water using the same surgical micropump. Retouching was extremely difficult and not very successful since the refractive index and gloss of the alkyd was different from the retouching paints. This is a problem that is also encountered with other glossy alkyd works.

The second example is a painting by Frank Stella, created in 1968, and listed as alkyd on canvas. The paint was applied directly to the canvas and has a matt surface, likely an interior alkyd house paint; the painting consists of two side-by-side sequences of colored bands that spiral to their centers. The alkyd paint in this case did not show any fragility issues since the paint was applied in a thin layer and was also partially absorbed into the unprepared canvas, but it presented dirt, marks, and residue of other materials. After a preliminary dry cleaning with Wishab sponges, the paint was wetted by the above-mentioned chelating solution, which did not cause any blooming effect. On the other hand, other solvents tested produced a lowering of the tone of the colors. The painting was successfully cleaned using a 1% sodium citrate aqueous solution, buffered to pH 6–7, and rinsed with distilled water, using Saugwunder suction block sponges.

CONCLUSIONS AND CONSERVATION RECOMMENDATIONS

The aged alkyd films, whether naturally or artificially aged, were brittle and difficult to handle. This is due to the high molecular weight of the alkyd polymer and faster stiffening from the excessive cross-linking and subsequent degradation reactions. As observed in the practical examples, the mechanical properties and damage can vary on the basis of the type of alkyd, the preparation of the support, and painting technique. Considering general conservation requirements, it is best to handle all alkyd paintings with care, especially those with flexible supports, since they can become very brittle over time. The majority of the problems observed come from the fatty acid component of the resin, so to limit these problems, alkyd paintings should also be stored in conditions similar to those used for oil paintings.

Another point to keep in mind is the potential pigment dependence on the long-term drying and aging behavior of these paints. This point warrants further study. Artists' alkyd paints are designed to be dry to the touch in 24 hours, regardless of the color, but it is clear from the results that it can take much longer for complete chemical drying (autoxidation) and that there are significant differences in T_g of the paints after years of drying.

When identifying and characterizing an alkyd paint using a Py-GC-MS technique, it is important to derivatize the sample since more polar molecular fragments may not elute from the column in all experimental conditions. Derivatization also

allows identification of the specific monomers used in the alkyd polymer and could also aid in identifying the brand or type of alkyd paint. For artists' alkyds, Winsor & Newton used resins containing phthalic acid, whereas the Ferrario and the Da Vinci Paint Co. used resins containing isophthalic acid. The PDQ paints contained both types of resins. However, it should always be assumed that the exact formulations of the paints are unknown, because there is a possibility of polymer or additive variations over the years, as well as a change in raw material distributors.

Acknowledgments

The Winsor & Newton Artists' Alkyd Colours (discontinued) and Griffin Alkyds samples cast in 1980 and 1999, respectively, were provided by M. F. Mecklenburg at the Smithsonian Institution (Museum Conservation Institute). The Winsor & Newton alkyd resin reference was provided by A. Foster, Winsor & Newton. The PDQ paints samples were provided by the Modern Materials Collection and Study Center of the National Gallery of Art, Washington, D.C. The conservation treatments (practical examples) of paintings with alkyds were carried out by Barbara Ferriani, a private conservator in Milan, Italy. The authors kindly thank both the Smithsonian Institution and the National Gallery of Art for the historic artists' alkyd samples and Barbara Ferriani for her availability to share her results.

REFERENCES

Erhardt, D., C. S. Tumosa, and M. F. Mecklenburg. 2005. Long-Term Chemical and Physical Processes in oil Paint Films. *Studies in Conservation*, 50:143–150.

Fuesers, O. 2006. Zum Einfluss organischer Lösemittel auf die mechanischen Eigenschaften von Alkydharz– und Ölfarbe. [The Influence of Organic Solvents on the Mechanical Properties of Alkyd Resin- And Oil Paint.] Diploma thesis, Hochschule der Künste Bern, Bern.

Fuesers, O., and S. Zumbühl. 2008. "The Influence of Organic Solvents on the Mechanical Properties of Alkyd and Oil Paint." Paper presented at 9th International Conference on NDT of Art, Jerusalem, Israel. http://www.ndt.net/article/art2008/papers/219Fuesers.pdf (accessed 25 May 2010).

Lack, C. 1988. Performance and Working Properties of Artists' Alkyd Paints. M.A.C. thesis, Faculty of Arts and Science, Queen's University, Kingston, Ontario, Canada.

Lazzari, M., and O. Chiantore. 1999. Drying and Oxidation Degradation of Linseed Oil. *Polymer Degradation and Stability*, 65:303–313. http://dx.doi.org/10.1016/S0141-3910(99)00020-8.

Mallégol, J., J. Gardette, and J. Lemaire. 2000. Long-Term Behavior of oil-Based Varnishes and Paints. Photo- and Thermo-oxidation of Cured Linseed Oil. *Journal of the American Oil Chemists' Society*, 77(3):257–263. http://dx.doi.org/10.1007/s11746-000-0042-4.

Muizebelt, W. J., J. C. Hubert, and R. A. M. Venderbosch. 1994. Mechanistic Study of Drying of Alkyd Resins Using Ethyl Linoleate as a Model Substance. *Progress in Organic Coatings*, 24:263–279. http://dx.doi.org/10.1016/0033-0655(94)85019-4.

O'Neill, L. A. 1970. "Chemical Studies on the Degradation of Oil and Alkyd Media." In *X. FATIPEC Kongressbuch*. [Proceedings of the 10th FATIPEC Congress.], pp. 225–229. Weinheim, Germany: Verlag Chemie.

Patton, J. C. 1962. *Alkyd Resin Technology*. New York: Interscience.

Ploeger, R., S. Musso, and O. Chiantore. 2009a. Contact Angle Measurements to Determine the Rate of Surface Oxidation of Artists' Alkyd Paints during Accelerated Photo-ageing. *Progress in Organic Coatings*, 65:77–83. http://dx.doi.org/10.1016/j.porgcoat.2008.09.018.

Ploeger, R., D. Scalarone, and O. Chiantore. 2008. The Characterization of Commercial Artists' Alkyd Paints. *Journal of Cultural Heritage*, 9:412–419. http://dx.doi.org/10.1016/j.culher.2008.01.007.

———. 2009b. Thermal Analytical Study of the Oxidative Stability of Artists' Alkyd Paints. *Polymer Degradation and Stability*, 94:2036–2041. http://dx.doi.org/10.1016/j.polymdegradstab.2009.07.018.

Saunders, K. J. 1973. *Organic Polymer Chemistry*. London: Chapman and Hall.

Schilling, M. R., J. Keeney, and T. Learner. 2004. "Characterization of Alkyd Paint Media by Gas Chromatography–Mass Spectrometry." In *Modern Art, New Museums: Preprints of the IIC Bilbao Congress*, ed. A Roy, and P. Smith, pp. 197–201. London: International Institute for Conservation.

Sonoda, N. 1998. Application des méthodes chromatographiques à la caractérisation des peintures alkydes pour artistes. [Application of Chromatographic Methods for the Characterization of Alkyd Paints for Artists.] *Techne*, 8:33–43.

Staples, P. 1982a. Master Classes in Alkyd: The Drying Performance. *The Artist*, 97(2):17–19.

———. 1982b. Master Classes in Alkyd: The Development of Alkyd Colours. *The Artist*, 97(1):11–14.

van Gorkum, R., and E. Bouwman. 2005. The Oxidative Drying of Alkyd Paint Catalysed by Metal Complexes. *Coordination Chemistry Reviews*. 249:1709–1728.

The Nonideal Action of Binary Solvent Mixtures on Oil and Alkyd Paint: Influence of Selective Solvation and Cavitation Energy

Stefan Zumbühl , Ester S. B. Ferreira, Nadim C. Scherrer, and Volker Schaible

ABSTRACT. Cleaning strategies in restoration and conservation often involve the use of solvent mixtures, despite the fact that the interaction between these and the objects under treatment is not always well known. Binary solvent mixtures behave nonideally; that is, the properties are not directly proportional or related to the mixing ratio. This fact contradicts the trivialized solubility charts, for example, the Teas chart, known and applied in practical restoration. The description of the dissolving action of binary systems therefore requires additional information such as the solvation and solubilization mechanisms involved. The effects of binary solvent mixtures on oil and alkyd paints were systematically investigated, with particular focus on the swelling action and leaching of binding media components. In total, 75 binary mixtures made from the solvents *n*-hexane, toluene, chloroform, diethyl ether, acetone, and ethanol were experimentally applied to free paint films by immersion. The solvation was studied by application of the linear solvation energy relationship based on Catalán's solvatochromic system. Extracted components were quantified gravimetrically and characterized with Fourier transform infrared spectroscopy, direct temperature-resolved mass spectrometry, and gas chromatography mass spectrometry. Selective solvation is observed both in oil and alkyd paints, but to a variable extent. The nonideal action of solvent mixtures, however, arises primarily from a lowering of the cavitation energy within the liquid by the formation of associates. This effect is thus a solute-independent process, which raises the entropy of mixing. As a consequence, many of the solvent mixtures tested had a far more detrimental effect on the paint films than the pure solvents.

Stefan Zumbühl *and* ***Nadim C. Scherrer****, Art Technological Laboratory, Bern University of Applied Science Fellerstrasse 11, CH-3012 Bern, Switzerland.* ***Ester S. B. Ferreira****, Scientific Laboratory, Swiss Institute for Art Research Zollikerstrasse 32, CH-8032 Zurich, Switzerland.* ***Volker Schaible****, Department of Restoration, The Stuttgart State Academy of Art and Design, Am Weissenhof 1, D-70191 Stuttgart, Germany. Correspondence: stefan.zumbuehl@bfh.ch.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

INTRODUCTION

The use of solvent mixtures for surface cleaning in restoration and conservation is widespread despite the lack of knowledge on the true consequences of such a treatment. Recently, azeotropic solvent mixtures have been proffered in particular (Saunders, 2008; Augerson, 2005). It is well known that binary solvent mixtures behave nonideally, which means that the properties of the mixture are neither proportional nor related to the mixing ratio. The solubility of a material is controlled by the solubilization of the solute and the molecular stabilization of the solute (dissolved solid) within the liquid phase. There is a clear difference in behavior between a solvent mixture and either of the pure solvents as both their solvation properties and their cavitation energy

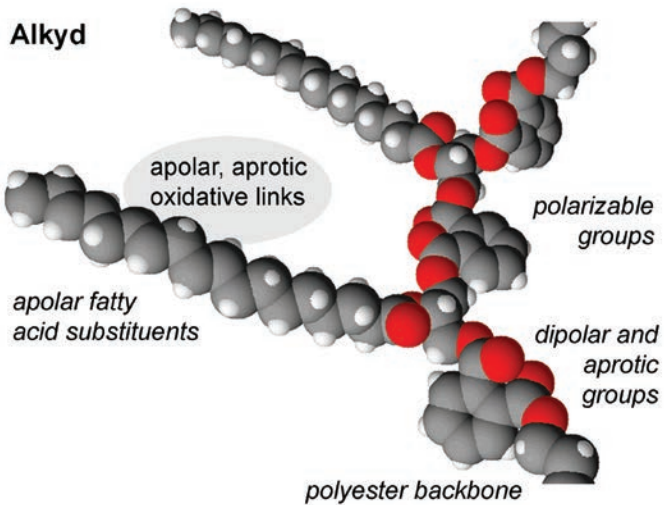


FIGURE 1. Model of a segment of an alkyd resin showing the phthalic acid polyester backbone and the fatty acid branches.

vary significantly. Solvation describes the intermolecular forces between solvent and solute, whereas selective solvation arises from a greater affinity of one component of the solvent mixture to the macromolecules or other components of the paint film (Marcus, 2002). Of particular interest in a practical context is cosolvation, where each solvent exhibits a selective affinity to one type of structural element. This may lead to the increased solubility of a bistructural material such as the alkyd paints, which contain a phthalic acid polyester backbone and fatty acid substituents (Figure 1).

The cavitation energy, which is a physical property of liquids, has often been ignored. Looking at the solubilization in energetic terms, the following equation must be taken into account (Reichardt, 1990):

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

In a dissolution process the free energy of mixing ΔG_m must be lowered upon solubilization. The enthalpy of mixing ΔH_m, which corresponds to the commonly known rule of "like dissolves like," requires similar intermolecular solvent-solvent and solvent-solute forces for successful action and is mostly positive and small (Reichardt, 1990). Therefore, the entropy of mixing ΔS_m at a given temperature T is of relevance. It can be calculated using the Flory-Huggins model of thermodynamics of polymer solubility (Flory, 1942; Huggins, 1942). The change in entropy is largely dependent on the strength of the intermolecular interaction within the liquid because the liquid cohesion has to be overcome to form a cavity in the liquid to incorporate the solute (Chipperfield, 1999). Cavity formation can be described by the cohesive energy of the liquid and can be qualified by the Hildebrand parameter δ_H^2, a parameter that controls the entropy of the dissolution process. This process of dissolution comprising both endo- and exothermic steps is schematized in (Figure 2). The exothermic step, an enthalpic process, can be described by the intermolecular interaction between solute and solvent. These can be dispersive, aprotic, or protic interactions.

Thus, the weaker the cohesive forces within a liquid are, the better the material solubilization is. The so-called cavitation energy is of direct relevance since the energy of cohesion is constant in pure solvents but varies strongly in solvent mixtures (Marcus, 2002).

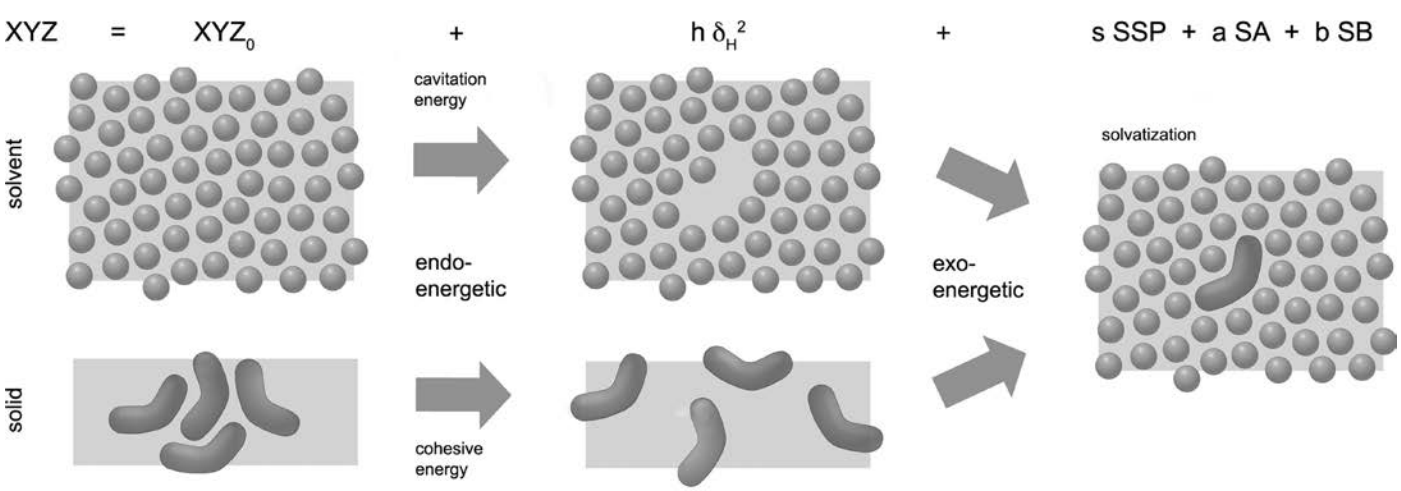


FIGURE 2. Schematic representation of the two-step dissolution process. The first endoenergetic step represents the cavity formation. The exoenergetic step corresponds to the intermolecular interactions between solute and solvent, i.e., SSP, dispersive; SB, aprotic; SA, protic interactions.

METHODS

The study of the effect of solvent mixtures on commercial oil and alkyd paints focused on the behavior of the cross-linked matrix upon solvation, the solubility, and leachability of low molecular weight compounds. Paint products used were Schmincke Norma Professional-Ölfarbe 11704, PBk 9, 37 mL and Winsor & Newton Griffin alkyd paint 1302340, PBk 9, 37 mL at a film thickness of 300 mm. The alkyd tested is a long-oil *o*-phthalic acid polyester derivative often used in oxidative drying of alkyd paints (Ploeger, 2009). The paint films were aged over 12 months while applying True-Lite 5500 K daylight under window glass at 35°C–40°C. Because of the similarity of the chemical nature of the binders in these paints it was possible to compare selective solvation effects. The experiments were run with six solvents exhibiting characteristic interactive properties, *n*-hexane, toluene, chloroform, diethyl ether, acetone, and ethanol (pure, Merck), as well as binary mixtures thereof at five different molar mixing ratios, 0.15:0.85, 0.35:0.65, 0.50:0.50, 0.65:0.35, and 0.85:0.15, in correspondence to data collected by Marcus (2002). Swelling tests were performed after Zumbühl (2005). The swelling capacity upon immersion was used to quantify solvation effects on the binder matrix and explore its relation to the parameters of the solvent mixtures. The linear solvation energy relationship based on the solvatochromic system developed by Catalán (2001) was applied to characterize the solvent mixtures. A PerkinElmer LAMBDA 750 UV/Vis/NIR spectrometer was used at a spectral resolution of 1 nm to quantify the extraction of binding media components from leachates of alkyd paint films immersed in 25 binary ethanol mixtures for 1 and 10 minutes (maximum swelling). Extracts of 2 g of paint sample in 50 mL of solvent were gravimetrically quantified and characterized using Fourier transform infrared spectroscopy (FTIR), direct temperature resolved mass spectrometry, and gas chromatography mass spectroscopy. The FTIR measurements were performed on a PerkinElmer System 2000 and a Bruker HYPERION 3000/Tensor 27 at 4 cm^{-1} spectral resolution and 32 scans. For spectroscopic distinction of the carboxylic acid groups from other oxidation products, samples were rolled out on CVD diamond windows and exposed to sulfur tetrafluoride (SF_4) for 16 hours in a Teflon chamber (Mallégol et al., 2000). Direct temperature-resolved mass spectrometry (DTMS) measurements were carried out on a Thermo DSQ II quadrupole instrument equipped with a direct probe module. The sample was homogenized in methanol (2 mL to 1 mg of sample). Approximately 0.5 mL of the suspension (equivalent to 0.25 mg sample) was applied to the rhenium filament, and the solvent was allowed to evaporate. The filament was then introduced into the ion source and resistively heated by ramping the applied current. (Probe experimental parameters were as follows: 5 s at 0 mA, ramp 10 mA/s to 1000 mA, and 20 s at 1000 mA. Mass spectrometer parameters were as follows: ion source temperature, 220°C; electron lens, 100 V; electron energy, –16 eV; emission current, 45 mV; lens 1, –25 V; lens 2, –8 V; lens 3, –25 V; prefilter –12.5 V; full scan mode mass to charge ratio *m/z*, 42–1050; scan rate, 9700 amu/s.) Analyses were carried out in triplicate.

RESULTS AND DISCUSSION

The solvation properties were characterized by analyzing the swelling behavior of free paint film, expressed in volume change $\Delta V/V_0$ (Zumbühl, 2005). The absolute swelling values are different for oil and alkyd paint. This is due to distinct densities within the cross-linked system and variable mobility of the polymer chains. All 75 binary solvent mixtures within the 15 experimental series exhibited nonideal properties (Figure 3).

Nonideal swelling properties of ethanol mixtures were similarly documented by Phenix (2002). In order to qualify the selective solvation, the parametrization of the solvent mixtures was carried out using the Catalán (2001) solvatochromic linear solvation energy relationship system. Results show that solvation of oil paint systems is dominated by dispersive interactions, whereas dipole-dipole interactions as well as specific protic and aprotic interactions are of negligible importance. The solvation of the oxidative functional groups is only of minor influence. This is also true for mature oil paint films, where the absolute swelling capacity decreases with age while the relative solvent sensitivity remains nearly unchanged (Stolow, 1978). Cosolvation was observed in alkyd paint systems exhibiting a very distinct swelling sensitivity when compared to oil paint. This can be explained through dipolar solvents, e.g., acetone, showing a dipole-induced interaction with polarizable functional groups, such as aromatic rings and ester groups within the phthalic acid polyester structure of the alkyd. The nonideal swelling properties, however, cannot be due to selective solvation because no relation between these two factors was observed.

Nonideal Action of Solvent Mixtures

The swelling data reveal almost equivalent swelling anomalies within oil and alkyd paints. In extremis, the swelling volume can reach several times the ideal value, as shown in Figure 3. It seems obvious that this effect is not influenced by the liquid-solid interactions but is unambiguously caused by liquid-liquid interactions. As a general rule, the larger the difference in polarity is between the mixed solvents, the greater the observed deviation is from the ideal behavior. In apolar mixtures this deviation from ideal behavior is generally small. In contrast, mixtures containing a polar solvent deviate significantly and may exhibit strong anomalies in the swelling behavior (Figure 4).

As a consequence, all ethanol mixtures induce very strong swelling anomalies in oil and alkyd paints, with an increase in volume of up to 200%. This effect is particularly pronounced with ethanol mixtures forming azeotropes, an observation that is consistent with the findings for different polymers: here the solubility increases if at least one of the components strongly interacts

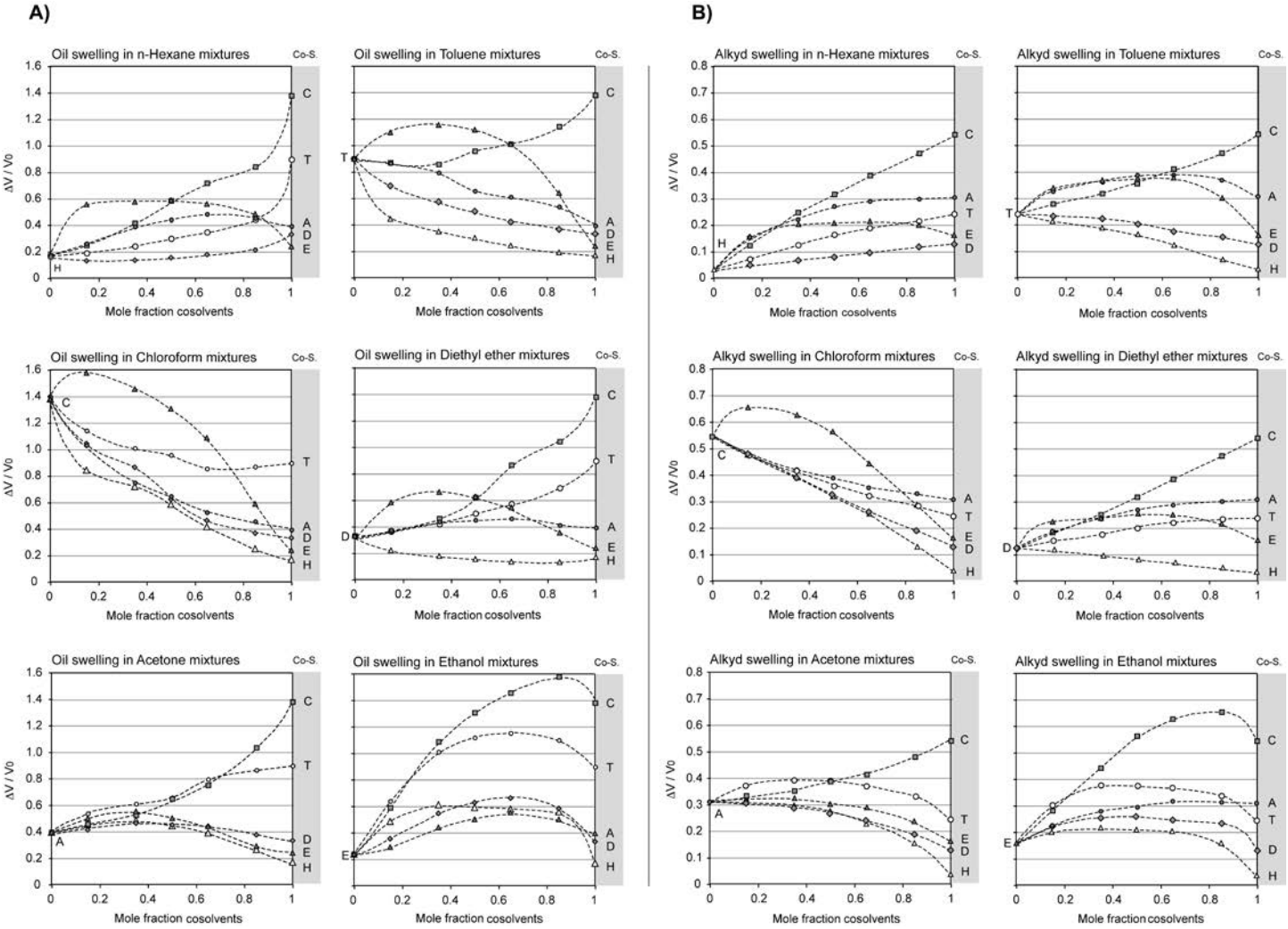


FIGURE 3. Swelling of (A) oil paint and (B) alkyd paint in binary solvent mixtures. All series exhibit nonideal behavior. Cosolvents (Co-S.) are H, *n*-hexane; T, toluene; C, chloroform; D, diethyl ether; A, acetone; and E, ethanol.

with the polymer even though it is virtually incompatible with the cosolvent (Wessling, 1970). These swelling anomalies conspicuously correlate with a change in boiling point (Hellwege, 1975) or the exceed volume V^E (Fermeglia and Lapasin, 1988) of binary mixtures. In turn, this correlation can be explained by a change in cohesive properties (Figure 5).

These anomalies occur when the intermolecular interaction between the individual components is smaller than that between structurally similar molecules. The formation of associates of the polar solvent component within the mixed system leads to a local reduction in the cohesive energy between liquid clusters of variable nature. Such mixtures can be described as microheterogenic systems (Murdoch et al., 2002). From the perspective of an energy landscape (Abraham et al., 2007), the system represents basins with lower cohesive energy between the solvent phases (Figure 6).

Since energy minima are necessary for cavity formation, the distribution of the solute in the surrounding liquid is, in general, preferential in microheterogeneous mixtures. Thus, even very small amounts of ethanol in an arbitrary binary solvent mixture can dramatically increase the swelling action. The opposite applies in the case of an increase in cohesive energy (Sivakumar and Naidu, 1997). This is evident, for example, in the case of acetone-chloroform mixtures, where the interaction between the molecules of the different solvents forming hydrogen bonds is much stronger than between molecules within the individual solvents. No cluster effects can thus be observed. As a result, the nonideal behavior of solvent mixtures is dominated by intermolecular forces within the liquid and therefore is largely independent of the solvation process.

Leaching Capacity of Solvent Mixtures

The properties of solubilization discussed above and the swelling capacity of solvent mixtures are directly relevant to the

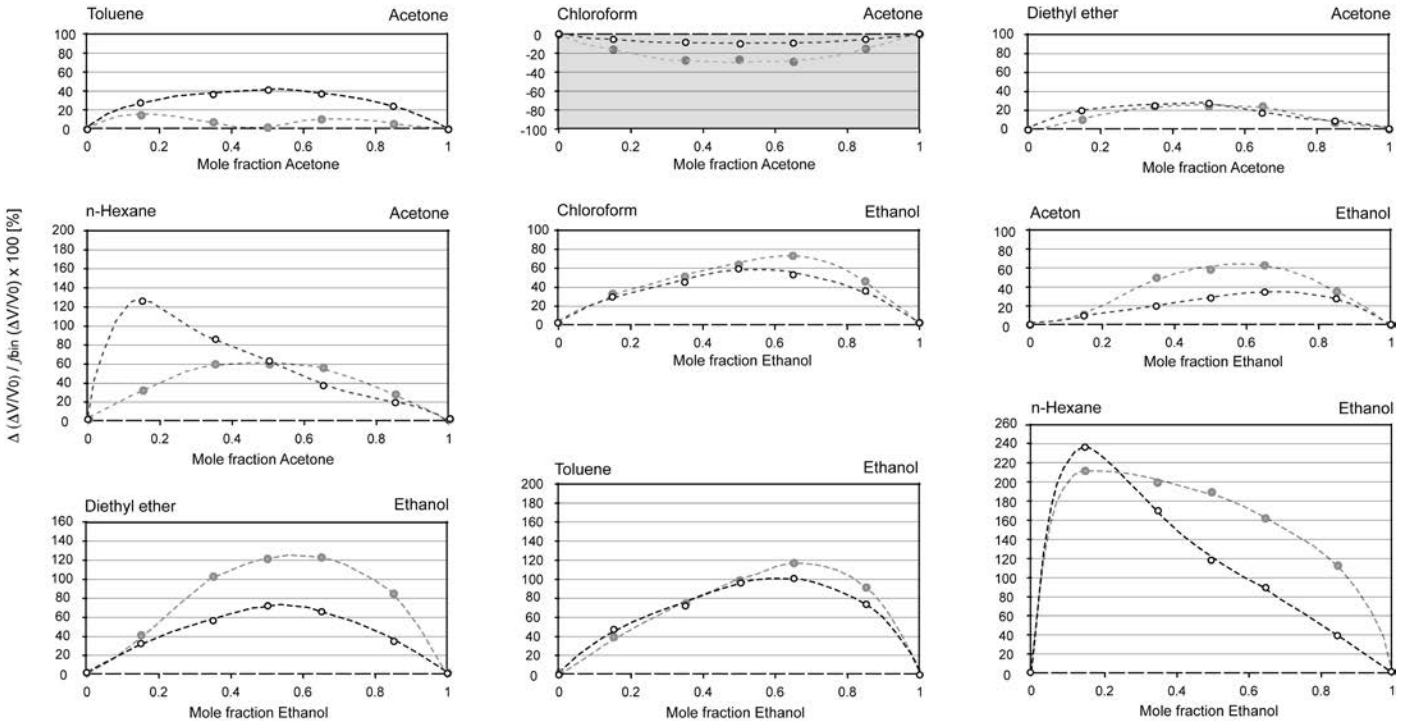


FIGURE 4. Swelling anomalies of oil (shaded circles) and alkyd paint films (open circles) in solvent mixtures containing acetone and ethanol. Apart from the chloroform-acetone mixture (shaded gray), all series show positive anomalies. These mixtures thus have a significantly increased swelling capacity exceeding that of the pure solvents several times.

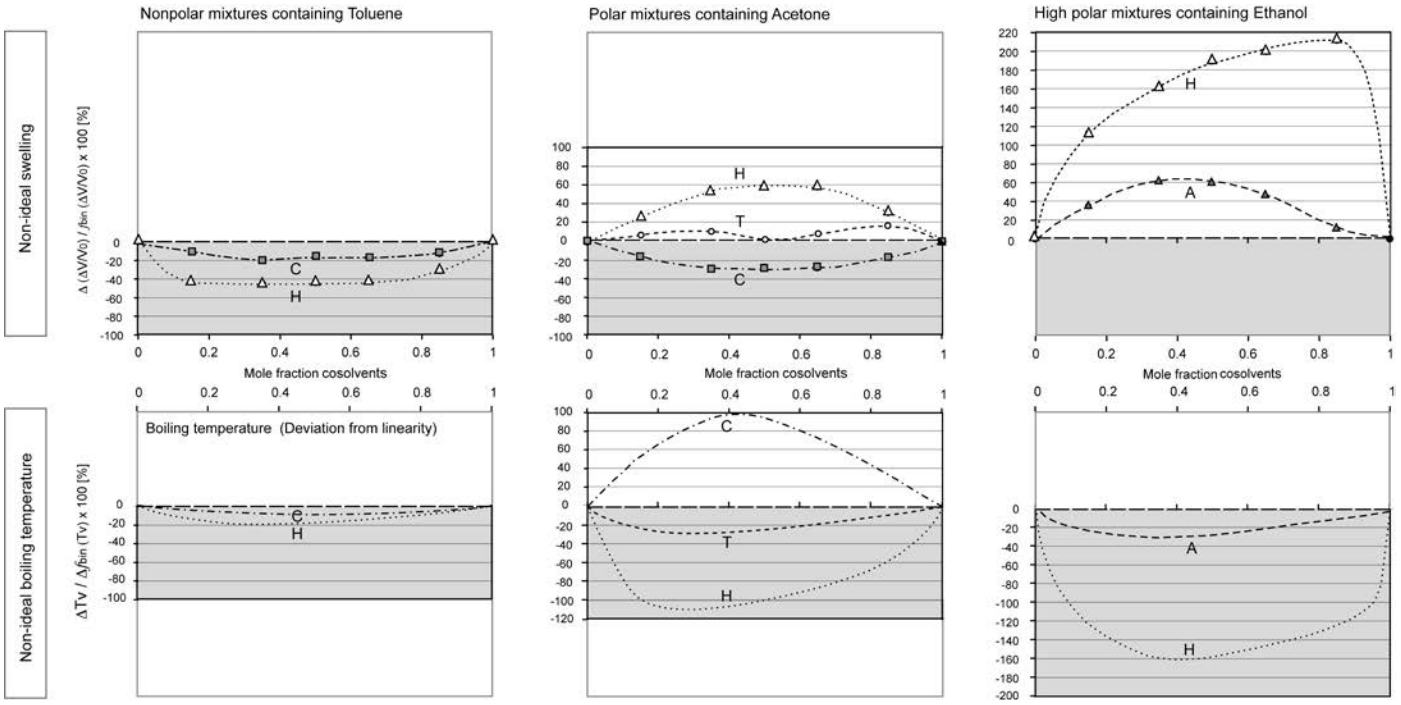


FIGURE 5. (top) Nonideal swelling of oil paint in relation to (bottom) the nonideal boiling temperatures of the binary mixtures. Mixtures containing polar solvents show an inverse relationship between boiling point and swelling behavior. Deviation from ideal behavior increases with an increase in polarity difference of the solvents mixed. Gray shading highlights negative anomalies.

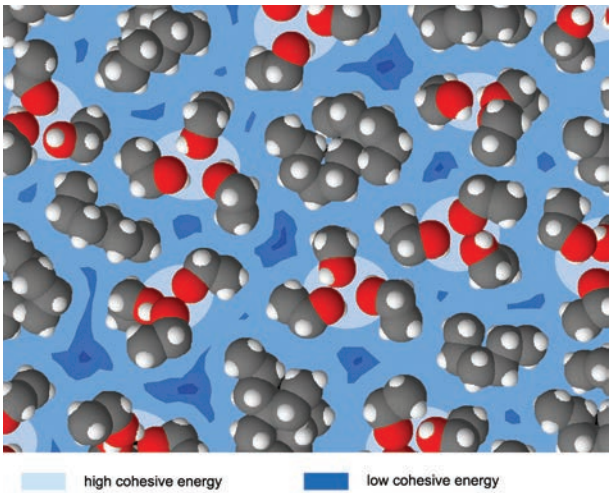


FIGURE 6. Schematic diagram representing the energy landscape of a binary mixture made from *n*-hexane and ethanol. Ethanol molecules cluster to form highly structured associates in a nonpolar environment. The reduced compatibility of the two liquids leads to locally reduced intermolecular interactions, which in turn form energy lows, or so-called energy basins, between the two phases.

extraction of low molecular compounds. Since oil and alkyd systems are structurally related, similar aging processes and degradation products are to be expected. For a full description on the nature of alkyds and their oxidative and hydrolytic degradation, the reader may refer to the chapter by Ploeger and Chiantore (this volume). Such compounds may comprise free fatty acids, dicarbonic acids, and oxidized products of fragmentation. These tend to be susceptible to leaching (Sutherland, 2001). On the basis of theory and published empirical data on leaching, mixtures containing ethanol are expected to have a destructive effect on oil and alkyd paints. Within this context, the extractive power of 25 binary mixtures of ethanol (with *n*-hexane, toluene, chloroform, diethyl ether, or acetone) applied to alkyd paint films was quantified. Experiments revealed that the nature and amount of extracted material is strongly dependent on the swelling capacity of the solvent mixture (Figure 7).

Several of these mixtures exhibited a leaching effect exceeding that of pure solvents. Not surprisingly, FTIR analyses suggest that increasing polarity of the solvent mixture results in increased leaching of polar oily components. The acidity of the extract was characterized by FTIR after SF_4 treatment. The higher the solvent polarity was, the more effective the leaching of polar material was. This is comparable to results published by Fuesers (2006). Furthermore, it was observed that the stronger the swelling was,

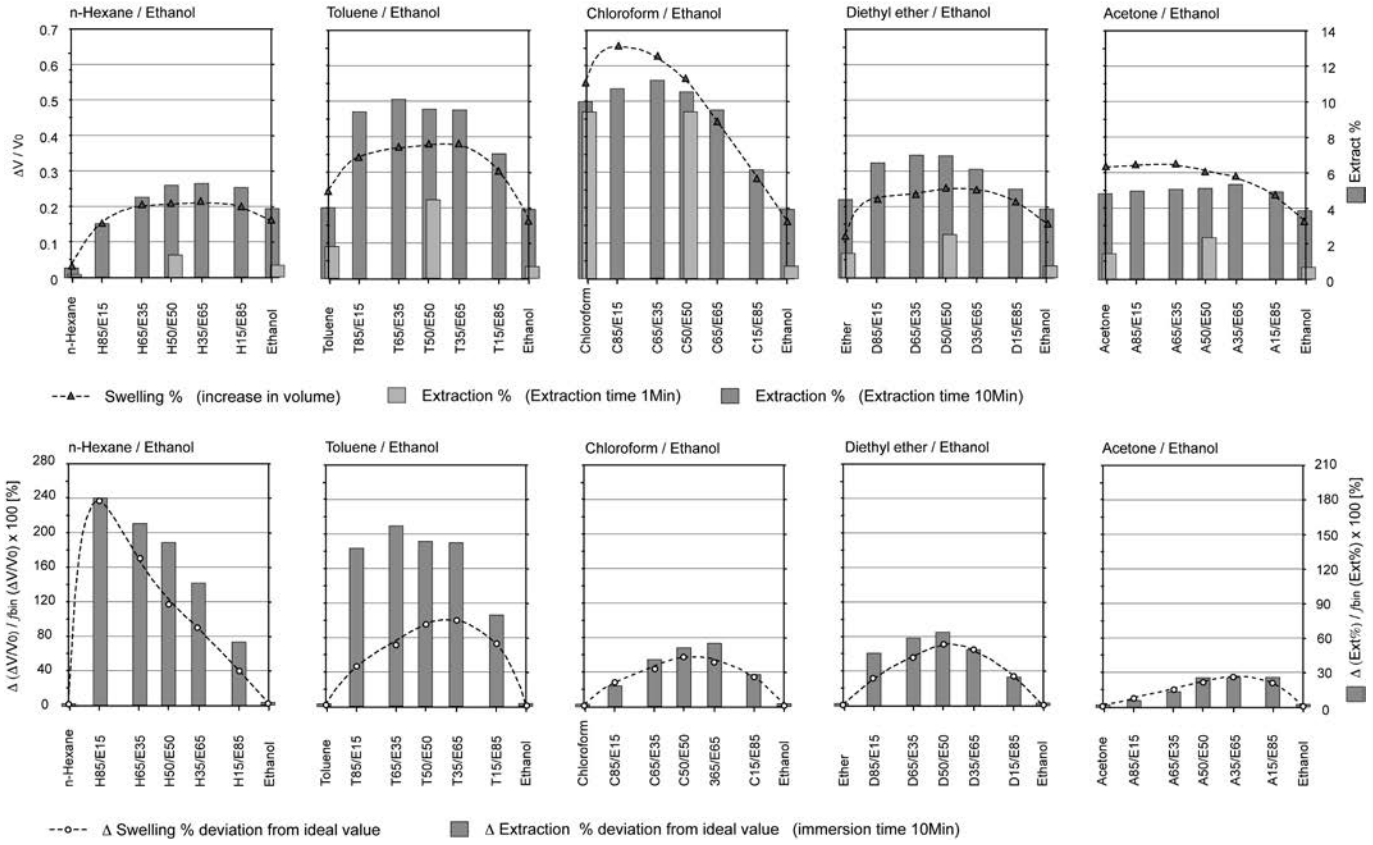


FIGURE 7. Weight percent of extracted material from alkyd paint (gray bars) versus swelling capacity (dotted line) in binary solvent mixtures with ethanol. (top) Absolute values. (bottom) Deviation from linear behavior.

the higher the amount of material extracted was. The main component leached overall was found to be a waxy rheological additive based on hydrogenated castor oil similar to Crayvallac Antisettle CVP produced by Cray Valley (Figure 8). This additive is often used in modern paint systems of low polarity and was also found by Ploeger (2009).

At swelling levels where changes in volume exceed 7 vol %, there was a massive increase of these triglycerides within the

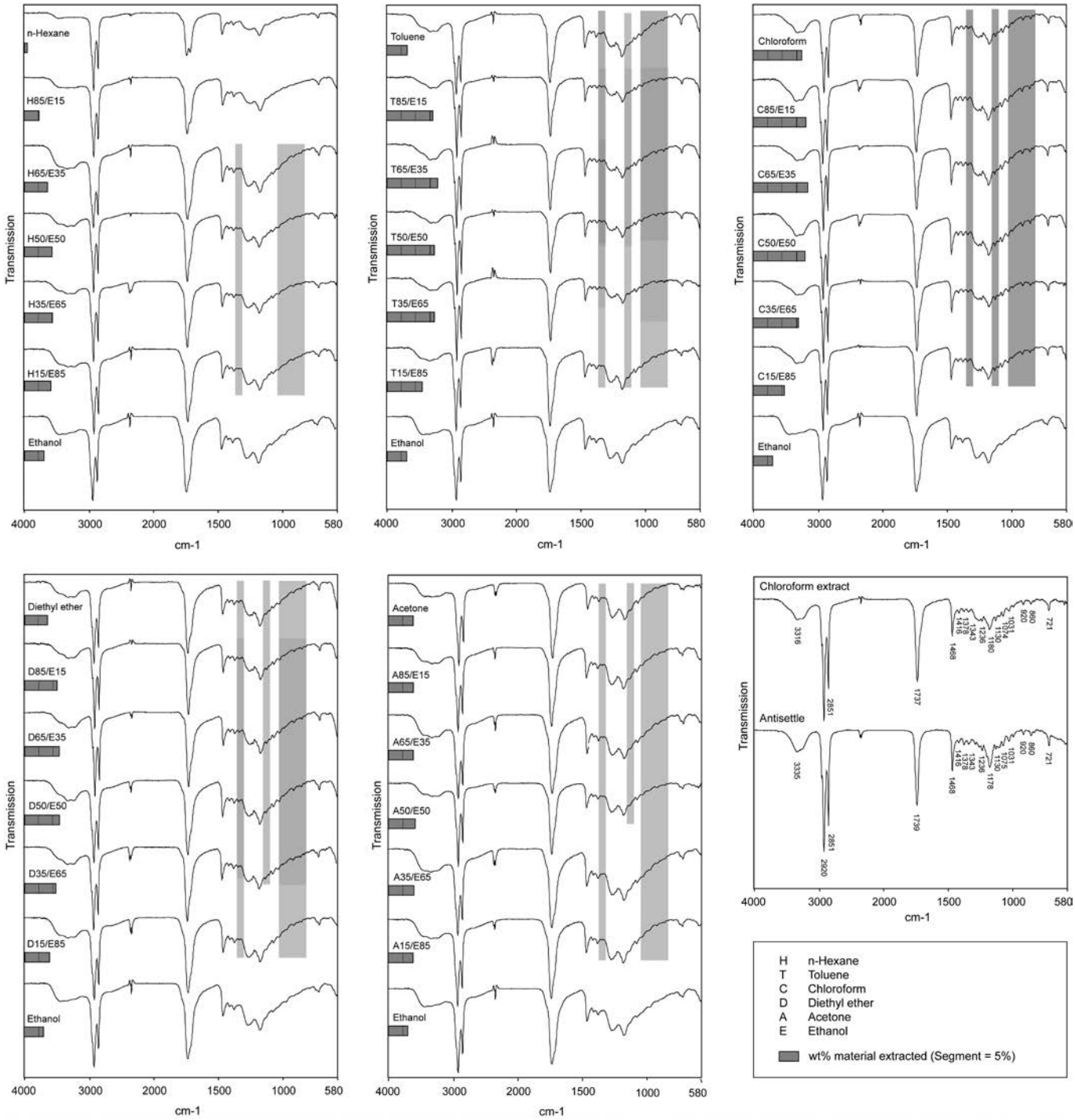


FIGURE 8. The FTIR spectra of dried extracts from alkyd paint films immersed in binary solvent mixtures with ethanol. The higher the swelling capacity is, the more paint additive is extracted. This is represented by a series of sharp signals (highlighted in grey). The additive was identified as a hydrogenated castor oil derivative (antisettle) used as a rheology modifier.

leachates. Since the leachability strongly depends on the swelling capacity of the matrix, binary mixtures of ethanol proved to be far more destructive than each of the individual pure components of the mixture.

DTMS Analysis of the Extracted Materials

Direct temperature-resolved mass spectrometry gives information on the general composition of relatively complex mixtures. The more volatile lower molecular weight fractions evaporate at lower temperatures while the more oxidized, cross-linked, and heavier material is progressively vaporized into the gas phase through a combination of evaporation and pyrolysis as the heating of the filament increases, In 2 minutes and 5 s analysis time different materials or types of materials are partially separated and analyzed. Learner (2004) has reported on the DTMS characterization of different materials found in oil and alkyd paintings.

The total ion chromatograms profiles of the extracts, with the exception of chloroform and hexane, show mainly three events (Figure 9A) at 0.50, 0.75, and 0.85 minutes. The first event is mainly characterized by *m/z* = 57, 60, 73, 98, 129, 157, 171, 185, 199, 213, 227, 256, 284, corresponding to the molecular ions and fragment ions of saturated fatty acids; it is also characterized by *m/z* = 84, 98, 111, 114, 124, 152, characteristic of diacids; *m/z* = 55, 83, 97, 264, indicative of unsaturated fatty acids; and *m/z* = 197, 215, characteristic of 12-hydroxy stearic acid, a component of castor wax. A number of peaks in this event, such as at *m/z* = 112, 126, 155, 167, remain unidentified. The main component in the second event is the castor wax rheology modifier (namely, characteristic fragment peaks at *m/z* = 536, 604, 507), and the third event is characterized by the presence of phthalates (*m/z* = 104, 148). As can be seen in Figure 9, in the case of the hexane extract, mainly fatty acids were found, whereas in the chloroform extract the main component was the castor wax rheology modifier, confirming the FTIR observations.

Castor wax is an industrial product resulting from the hydrogenation of castor oil. The main fatty acid components of the triacylglycerides present in castor oil are ricinoleic acid (12-hydroxy-9-*cis*-octadecenoic acid; 88%), linoleic acid (4.9%), oleic acid (3.5%), palmitic acid (1.4%), and stearic acid (0.9%). The final composition of the hydrogenated castor wax depends on

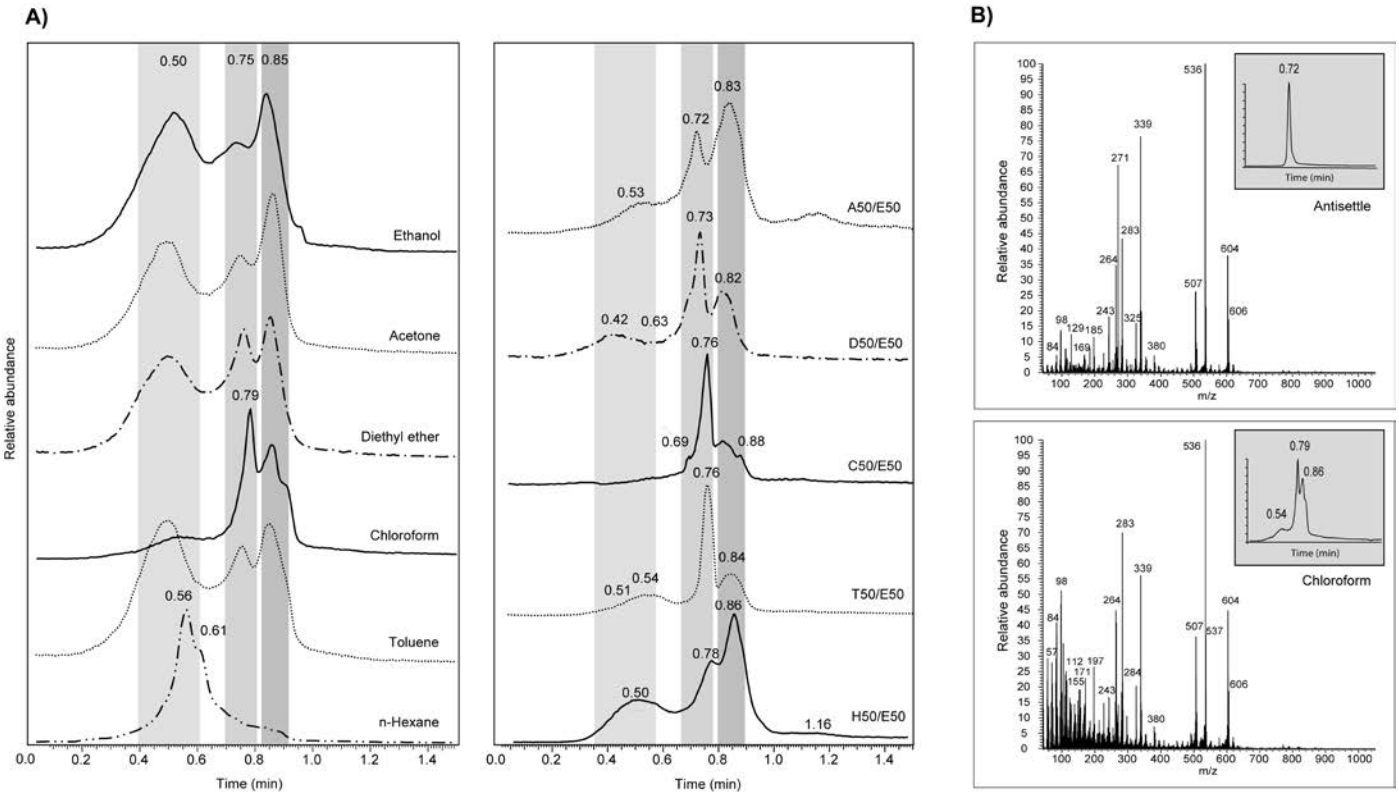


FIGURE 9. (A) Total ion chromatograms (TIC) of the 16 eV DTMS analysis of different pure solvents and solvent mixture dried extracts of light-aged alkyd paint. (B) EI 16 eV mass spectra of Crayvallac Antisettle CVP produced by Cray Valley. Average of the scans between 0.68 and 0.76 min (TIC in inset) and EI 16 eV mass spectrometric analysis of the dried chloroform extract of light-aged alkyd paint. Mass spectra of the second event (average of the scans between 0.74 and 0.82 min) and TIC in inset.

the hydrogenation conditions. Upon complete hydrogenation the main fatty acids are ketostearic acid (44%), hydroxystearic acid (12%), stearic acid (18%), oleic acid, and isomers (23%) and palmitic acid (2%) (Schneider et al., 2004). The total ion chromatogram of the commercial castor wax (Figure 9B) is characterized by a single event at 0.72 minutes of homogeneous composition and is dominated by the peak cluster peaks of the diacylglycerides at m/z = 536, 604, 507; monoacylglycerides at m/z = 339, 325; fatty acid fragments at m/z = 298, 271 (ketostearic acid), 283 (stearic acid), 282, 264 (oleic acid), 256 (palmitic acid); and smaller fragments from the fatty acid chain (m/z = 57, 60, 73, 129, 227, 243). By comparison, the same diacylglyceride fragments (m/z = 507, 536, 604) can be seen in the main event of the DTMS analysis of the chloroform extract, confirming castor wax as an important component of the paint fraction extracted by chloroform.

CONCLUSIONS

These experiments demonstrate that the nonideal action of solvent mixtures can be attributed to their physical properties, especially to the heterogenic free volume distribution. The influence of the cavitation energy was found to be far more relevant than that of cosolvation. Therefore, the swelling anomalies in solvent mixtures are comparable in oil and alkyd paints. The lowering of the cohesive energy in binary solvent mixtures is strongly dependent on the difference in polarity between the two solvent components as a consequence of the associate formations. The energy gap between the solvent clusters in microheterogenic liquids has a positive influence on the cavity formation and therefore on the change of entropy of the solubilization process, which can be described as the ease of distributing the solvated solute in the surrounding liquid. As a consequence, large amounts of paint additives were extracted because the leaching capacity generally correlates with the swelling action of specific solvent mixtures. Finally, a correlation between the kind of extracted material and the solvent polarity was found. In conclusion, it can be stated that, generally, solvent mixtures containing ethanol applied to alkyd paints had clearly a more damaging effect than either of the individual solvents making up the mixture.

REFERENCES

Abraham, S. E., D. Chakrabarti, and B. Bagchi. 2007. Energy Landscape View of Nonideality in Binary Mixtures. *Journal of Chemical Physics,* 126:074501. http://dx.doi.org/10.1063/1.2434967.

Augerson, C. 2005. Tips on Using Azeotropes for Cleaning Solvents and Adhesive Delivery. *AIC Paintings Specialty Group, Postprints,* 17:113–120.

Catalán, J. 2001. "Solvent Effects Based on Pure Solvent Scales." In *Handbook of Solvents*, ed. G. Wypach, pp. 583–616. New York: ChemTec Publishing.

Chipperfield, J. R. 1999. *Non-aqueous Solvents*. Oxford: Oxford University Press.

Fermeglia, M., and R. Lapasin. 1988. Excess Volume and Viscosities of Binary Mixtures of Organics. *Journal of Chemical and Engineering Data,* 33:415–417. http://dx.doi.org/10.1021/je00054a008.

Flory, P. J. 1942. Thermodynamics of High Polymer Solutions. *Journal of Chemical Physics,* 10:51–61. http://dx.doi.org/10.1063/1.1723621.

Fuesers, O. 2006. Zum Einfluss organischer Lösemittel auf die mechanischen Eigenschaften von Akydharz- und Ölfarben. Diploma thesis, Berner Fachhochschule, Bern.

Hellwege, K.-H. 1975. "Landolt-Börnstein—Numerical Data and Functional Relationships in Science and Technology, New Series, Group IV: Macroscopic and Technical Properties of Matter." In *Thermodynamic Equilibria of Boiling Mixtures*, Volume 3, ed. J. Weishaupt, pp. 1–276. Berlin: Springer-Verlag.

Huggins, M. L. 1942. Thermodynamic Properties of Solutions of Long-Chain Compounds. *Annals of the New York Academy of Science,* 18:1–32. http://dx.doi.org/10.1111/j.1749-6632.1942.tb47940.x.

Learner, T. J. S. 2004. *Analysis of Modern Paints*. Research in Conservation. Los Angeles: The Getty Conservation Institute.

Mallégol, J., J. L. Gardette, and J. Lemaire. 2000. Long-Term Behaviour of Oil-Based Varnishes and Paints: Photo- and Thermooxidation of Cured Linseed Oil. *Journal of the American Oil Chemists' Society,* 77:257–263. http://dx.doi.org/10.1007/s11746-000-0042-4.

Marcus, Y. 2002. *Solvent Mixtures—Properties and Selective Solvation.* New York: Marcel Dekker.

Murdoch, K. M., T. D. Ferris, J .C. Wright, and T. C. Farrar. 2002. Infrared Spectroscopy of Ethanol Clusters in Ethanol-Hexane Binary Solutions. *Journal of Chemical Physics,* 116:5717–5724. http://dx.doi.org/10.1063/1.1458931.

Phenix, A. 2002. The Swelling of Artist's 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.

Ploeger, R. 2009. The Characterization and Stability of Artist's Alkyd Paint. Ph.D. thesis, University of Torino, Turin, Italy.

Reichardt, C. 1990. *Solvents and Solvent Effects in Organic Chemistry.* Weinheim, Germany: VCH Verlagsgesellschaft.

Saunders, L. E. 2008. Applying Azeotrope Solvent Mixtures to Cleaning Issues in the Treatment of Paintings. *AIC Painting Specialty Group, Postprints,* 20: 121–124.

Schneider, R. S. S., V. Z. Baldissarelli, F. Trombetta, M. Martinelli, and E. B. Camarão. 2004. Optimization of Gas-Chromatographic Mass Spectrometric Analysis for Fatty Acids in Hydrogenated Castor Oil obtained by Catalytic Transfer Hydrogenation. *Analytica Chimica Acta*, 505:223–226.

Sivakumar, K., and P. R. Naidu. 1997. Excess Molar Volume of Binary Mixtures of 1,1,1-Trichlorethan with Ketones and Esters at 303.15 K. *Fluid Phase Equilibria,* 127:173–180. http://dx.doi.org/10.1016/S0378-3812(96)03102-0.

Stolow, N. 1978. "Solvent Action." In *Conservation and Restoration of Pictorial Art*, ed. N. Bromelle and P. Smith, pp. 153–157. London: Butterworths.

Sutherland, K. 2001. Solvent Extractable Components of Oil Paint Films. Ph.D. thesis, University of Amsterdam, Amsterdam.

Wessling, R. A. 1970. The Solubility of Poly(Vinylidene Chloride) in Solvent Mixtures. *Journal of Applied Polymer Science,* 14:2263–2277. http://dx.doi.org/10.1002/app.1970.070140907.

Zumbühl, S. 2005. Illusion mit System: Das Lösemitteldreieck in der Praxis—Aspekte zur Charakterisierung der Wirkung von binären Lösemittelmischungen. *Zeitschrift für Konservierung und Restaurierung,* 19:253–262.

Sensitivity of Oil Paint Surfaces to Aqueous and Other Solvents

Hannah Tempest, Aviva Burnstock, Polly Saltmarsh, and Klaas Jan van den Berg

ABSTRACT. This paper investigates the sensitivity of modern commercially produced artists' oil paints to the use of aqueous and other solvents for cleaning. Water sensitivity has been observed in oil paintings where the paint has been used to create a great range of surface effects. It was reported in paint that exhibits efflorescence where fluctuations in environmental conditions or former treatments may have accelerated migration of degraded components to the surface of the paint film. The colored passages most frequently cited as problematic included ultramarine, cadmium yellows, chromium oxide green, and cobalt violet. Oil paint films, based on twentieth-century manufactured paints, with known proportions of pigments, stearates, aluminum hydroxide, hydrolyzed linseed oil, and hydrogenated castor oil in linseed oil were prepared and cured. After artificial aging, the paints were tested for water sensitivity. Ultramarine paints were the most sensitive to water applied by swab, followed by chromium oxide, whereas raw sienna was the least sensitive. The inclusion of linseed fatty acids and aluminum hydroxide increased the sensitivity of the paints to water. Aluminum stearate-containing paints swabbed with aqueous solvents exhibited localized stearic acid efflorescence. Ultramarine stearate-containing paints formed a paint-medium skin that was initially resistant to swabbing with water but contained water-sensitive paint beneath.

INTRODUCTION

The water sensitivity of modern paintings produced with commercial artists' oil paints is a phenomenon commonly encountered by conservators of twentieth-century paintings. Sensitivity to the use of aqueous and other solvents typically applied with a cotton wool swab during cleaning affects well-bound oil paint and can also occur in paint that has been applied straight from the tube, with no modifications, or in tube paints with artists' additions of materials such as non- or semidrying oils, waxes, or resins. The problem has been reported in passages of large, unvarnished, and unglazed modern oil painting, including Jasper Johns' *Untitled*, 1964–1965 (Stedelijk Museum, Amsterdam; Burnstock et al., 2007; Wijnberg et al., 2007), Karel Appel's *Les Animaux*, 1961 (Collection of the Netherlands Institute for Cultural Heritage [ICN]; Mills, 2008; Mills et al., 2008), and paintings by Robyn Denny, dating from the 1960s, at the Museu Calouste Gulbenkian, Lisbon (Gayler et al., 2008). Related case studies and technical analysis of water-sensitive oil paintings from the 1950s and 1960s are discussed in depth in a recent Courtauld Institute of Art student project (Tempest, 2009).

Dirt deposition may be patchy or even and can be particularly disfiguring on modern paintings, which may have no layer of protective varnish, a varied surface texture, different degrees of porosity in different areas, or a significant degree of impasto to trap surface

***Hannah Tempest**, National Gallery of Denmark, Sølvgade 48-50, DK-1307 Copenhagen, Denmark. **Aviva Burnstock**, Department of Conservation and Technology, Courtauld Institute of Art, Somerset House, Strand, London WC2R 0RN, UK. **Polly Saltmarsh**, London, UK. **Klaas Jan van den Berg**, Netherlands Cultural Heritage Agency, P.O. Box 76709, 1070 KA Amsterdam, Netherlands. Correspondence: Aviva Burnstock, aviva.burnstock@courtauld.ac.uk; Klaas Jan van den Berg, k.van.den.berg@cultureelerfgoed.nl.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

dirt. The softness and tack of a young, unvarnished oil paint film makes it especially susceptible to dirt accumulation.

There is a number of ways to approach the surface cleaning of unvarnished water-sensitive oil paintings. The course of action is generally dictated by the exact nature of the sensitivity: in some cases extreme sensitivity coincides with a whole range of solvents, polar and nonpolar; in other cases, sensitivity is limited to aqueous solvents only. In certain cases, generally in underbound matte paint films, sensitivity is related more to the mechanical action of swab rolling. Subtle distinctions between matte and glossy surface effects can easily be compromised by cleaning, and imbibed surface dirt can be extremely difficult to remove evenly. These challenges demand the development of new methods and materials for conservation of modern paint surfaces. This study further investigates the causes of the sensitivity of twentieth-century oil paintings to aqueous cleaning.

EXPERIMENTAL METHODS AND MATERIALS

Test Paints

Test paints, replicating basic formulations of modern manufactured artists' oil paints on the basis of present knowledge (technical information was obtained from Harding, Colart, and Old Holland), were prepared from raw materials and painted out in early 2008. The materials used were cold-pressed and alkali-refined linseed oil (combined in a ratio of 4:1), powdered pigments, hydrogenated castor oil (1%–10%), linseed fatty acids (2%–5%), aluminum hydroxide (5%–30%), aluminum stearate (2%–30%), and zinc stearate (2%–30%; in ultramarine only). Additives were incorporated into test paints at a range of proportions recommended for use in tube paints, from 2%–5% of aluminum stearate (Tumosa, 2001) to 20%–30%, which is significantly higher than generally found in commercial paints in order to identify trends in sensitivity and to test analytical detection limits.

Three pigments were chosen for the study on the basis of their various degrees of sensitivity as observed in dried oil paint films: ultramarine (three different shades: two fine and one coarse), chromium oxide green, and raw sienna. All materials were provided by Old Holland (http://www.oldholland.com) except for aluminum hydroxide and aluminum or zinc stearate, which were obtained commercially. Proportions of most powdered additives were measured by weight as a percentage of the dry content; in the case of linseed fatty acids and hydrogenated castor oil, stock solutions of a linseed oil mixture with 2% and 5% linseed fatty acids and 2%, 5%, and 10% hydrogenated castor oil by weight were substituted as the binding medium. All of the paint samples were mixed with an automatic muller provided by Old Holland, which mimics the action of the industrial three-roller steel mill used in factories. The oil content was varied with the aim of achieving a "buttery" consistency where possible (Figure 1).

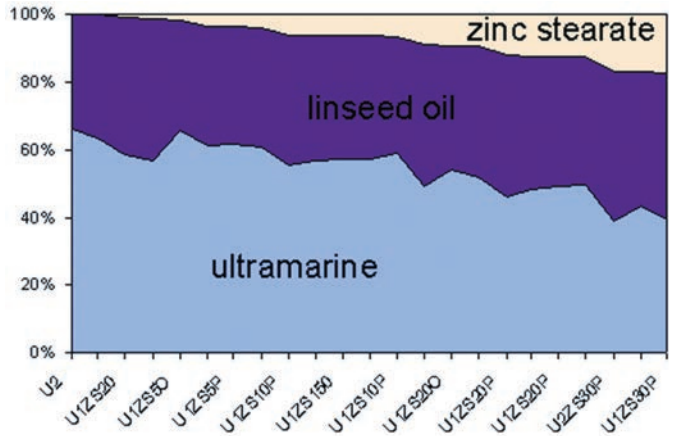


FIGURE 1. Graph showing the relative percentage by weight (vertical axis) of ultramarine pigment (light blue), drying oil (purple) and zinc steareate additive (cream) in test batches of paint. The percentage weight of zinc steareate additive increases from left to right in the graph from 0% to 30%. Note that the pigment content decreases as the zinc stearate increases from left to right, whereas the amount of oil remains relatively constant.

Ultramarine oil tube paints were painted out and aged, including a selection of Winsor & Newton, Michael Harding, Haagsche Kunstschildersverven Fabriek (no longer available), and Old Holland paints. Ultramarine, chromium oxide green, and raw sienna tube paints were modified with additives, combined in the automatic muller mixer, and painted out on thick Melinex and commercially prepared cotton canvas with chalk- and titanium white–containing acrylic priming. Each sample comprised a section of both flat and impasto paint, applied using a brush on canvas, a draw-down bar with a fixed clearance of 25μm for the flat area on Melinex, and a palette knife to create the impasto.

After three months of curing, artificial aging with fluorescent light tubes (36W Philips Color 96, in combination with Lexan polycarbonate sheets to filter out ultraviolet) of test paint films was carried out at about 44% RH and 25°C. The samples received the calculated equivalent of 25.2 years of museum lighting (200 lux, eight hours a day, assuming reciprocity). The samples were then stored under ambient conditions until testing at various times.

The paint films were tested for solvent sensitivity using the same procedures as in Mills et al. (2008). Tests were carried out after 6, 18, and 24 months of storage following artificial aging by three independent evaluators. The paint films were tested by swab rolling, applying minimal pressure, using deionized water, saliva, and iso-octane. Assessments were visually aided by light microscopy. The sensitivity criteria were categorized as follows: +++, very sensitive, pigment or paint removed within 5 swab rolls; ++, sensitive, paint removed within 10–20 swab rolls; +, moderately sensitive, paint removed within 30 swab rolls; –, not sensitive.

Analytical Methods

Cross sections were taken from test paint films and embedded in Polypol resin and dry polished. Elemental analysis was carried out with a scanning electron microscope with energy dispersive spectrometry (SEM-EDS) or X-ray microanalysis, and imaging was carried out in a variable-pressure SEM (VP-SEM). X-ray fluorescence was carried out with a portable instrument. Both X-ray diffraction and Fourier transform infrared (FTIR) analysis were carried out. The latter was also combined with an attenuated total reflection (ATR) system. Details of the equipment and operation conditions are given at the end of the paper.

RESULTS AND DISCUSSION

Conservators' Interviews

Interviews were conducted with conservators of modern paintings, including a survey that identified examples of water-sensitive oil paintings that ranged from unspecified paintings by Kandinsky and Malevich dating from the 1910s to works from the 1990s by John Murphy (P. Young, private practice, London, personal communication). The survey suggested that most of the water-sensitive paintings date from the 1950s and 1960s.

From the first decades of the twentieth century onward, paint formulations began changing, and numerous additives were being incorporated into manufactured oil paints for the first time (Tumosa, 2001). The limited number of documented occurrances of paintings sensitive to aqueous cleaning may be due to the application of protective varnish coatings to many paintings made before 1900. The peak in the noted occurrence of water sensitivity in paintings from the 1950s and 1960s may also relate to the recent treatment of the works in response to contemporary demands on the works for loan and display. Oil paintings from more recent decades may exhibit equal, or higher, degrees of sensitivity on aging; the extent to which they do may not be fully appreciated until they are brought into conservation studios in larger numbers in 20 or 30 years' time.

Unmixed tube colors were most frequently cited as problematic, for example, cadmium and chrome yellows and reds, ultramarine, cobalt blue, chromium oxide green, and purple pigments, such as cobalt violet (L. Wijnberg, Stedelijk Museum, personal communication; L. van der Loeff, Kröller-Müller Museum, personal communication; J. Krueger, National Gallery of Art, personal communication; S. Digney-Peer, Metropolitan Museum, personal communication; M. Basto, private practice, Lisbon, personal communication; Young, pers. comm.). Although water sensitivity is not usually noted in paints containing earth pigments, conservators tend to approach these passages with caution (Wijnberg, pers. comm.). Water sensitivity has been observed in oil paint films with a great variety of surface effects and application techniques; it is therefore very difficult to draw up diagnostic guidelines based on topography. However, there are some characteristic physical manifestations such as paint films with efflorescence that have been linked to water sensitivity (Basto, pers. comm.; Young, pers. comm.). In these cases, fluctuations in environmental moisture (or possibly previous cleaning campaigns) may have accelerated the migration of degraded components to the surface of the paint film. In other instances, sensitivity has been associated with unusually tacky paint; this commonly coincides with the modification of tube paints with artists' additions of other media but may also be associated with the plasticizing effect of metal stearates, as well as the low pigment volume concentration enabled by the inclusion of stearates.

Test Paint Films: Tests for Solvent Sensitivity

A summary of the test results with saliva are presented in Table 1. Tests with deionized water showed less sensitivity than those with saliva.

The most influential variable with regard to water sensitivity was found to be the pigment used for the test paints. Ultramarine films on canvas were consistently highly sensitive to deionized water and saliva (++, +++). The sensitivity of paints containing chromium oxide green depended on the batch and the admixtures with other materials (++, +, –), and raw sienna paints were the least sensitive (+, –). Chrome green and ultramarine paints on canvas showed a higher level of water sensitivity than the same films on Melinex. This may be attributed to the absorption of some of the oil binding medium and the formation of a less well bound paint film that was more susceptible to the mechanical action imparted by swabbing of the green and blue paint films. Conversely, raw sienna paint on Melinex showed moderate sensitivity (+) and was mostly insensitive on the canvas support (–). This difference in sensitivity was noted in the second set of tests that were carried out 18 months after the first.

In general, saliva was found to affect sensitive paint more quickly than deionized water. This may be due to the slightly higher pH (deionized water has pH 5.5; saliva has approximately pH 7.5), its surfactant properties, or its greater ionic strength. For ultramarine, the difference between water and saliva was less apparent than for the green and earth paints. The sensitivity of the paint films to iso-octane was generally low, but there was a consistent decrease in sensitivity of the chrome green and the raw sienna paints between 6 and 24 months after artificial aging, probably reflecting the further drying of the paint.

Ultramarine test paints in oil medium on canvas without additives were found to be very sensitive to saliva and water (+++, ++), and the commercial tube paints were invariably similarly sensitive. This relates to the hydrophilic nature of the pigment and the exacerbation of sensitivity through absorption of medium by the support that left the films more leanly bound. The addition of aluminum stearate to ultramarine and oil seemed to have little or no discernible effect on the sensitivity of the paints; the addition of zinc stearate reduced the sensitivity, especially in the second series of tests. Interestingly, the combined addition of aluminum stearate and aluminum hydroxide produced films

TABLE 1. Results of the cleaning tests with saliva after 6 and 24 months storage at ambient conditions after artificial aging. The results are mean category values of all tests carried out. No distinction is made between the different ultramarine pigments used since their sensitivities were similar. Symbols and abbreviations are as follows: +++, very sensitive, pigment or paint removed within 5 swab rolls; ++, sensitive, paint removed within 10–20 swab rolls; +, moderately sensitive, paint removed within 30 swab rolls; –, not sensitive; AS, aluminum stearate; AH, aluminum hydroxide; LF, linseed fatty acids; HC, hydrogenated castor oil; NT, not tested. An asterisk (*) indicates lower sensitivity at higher concentrations.

Pigment	Support	Testing time (months)	No additive	Al stearate	Zn stearate	Al hydroxide	AS/AH	LF	HC	LF–HC
Chrome green	Melinex	6	NT	+	NT	+/–	–	–	+/–	–
	Melinex	24	NT	–	NT	+/–	–	+/–	–	–
	Canvas	6	–	+/–	NT	+/–	–	+	++/+	++
	Canvas	24	+/–	+/–	NT	+	–	+/++	+	++
Ultramarine	Melinex	6	+	++*	++*	+	–	+	++/+	+/–
	Melinex	24	–	++/+*	+*	++/+	–	+/–	++	+
	Canvas	6	+++	+++/++*	+++*	+++	++	+++	+++	+++
	Canvas	24	+++/++	+++/++*	++*	+++	++	+++/++	+++	+++
Raw Sienna	Melinex	6	+/–	–	NT	+/–	–	+/–	–	–
	Melinex	24	+	+/–	NT	+	+	+	+	+
	Canvas	6	+/–	–	NT	+/–	–	–	–	+/–
	Canvas	24	–	+/–	NT	–	–	+/–	+/–	–

that were more resistant to saliva and water, most notably on Melinex (–). The addition of zinc stearate in combination with aluminum hydroxide had a similar but less pronounced effect.

Ultramarine on canvas with added aluminum hydroxide, linseed fatty acids (LF), and hydrogenated castor oil (HC) were significantly water sensitive (+++), also after prolonged aging. In contrast, on Melinex supports ultramarine paint without additives and films with added LF or LF and HC were significantly less sensitive (+, –) to saliva than the other ultramarine paints (++, +).

The three grades of ultramarine behaved differently. Test paints combining the two finer grades of ultramarine (36 and 37), oil, and 10% aluminum hydroxide produced paint films of closely similar appearance, with an even midlevel gloss and saturation in flat areas and saturated, slumped, and wrinkled impasto. The same recipe with ultramarine 244 resulted in a streaky flat area with distinct phase separation and a paint-medium skin (Figure 2), with slumping and wrinkling in the impasto and slight bloom in the interstices. In paints of the same recipe that substituted the three ultramarines, the coarser grade (244) was more sensitive to aqueous solvents but less sensitive to iso-octane than ultramarines 36 and 37.

Ultramarine has a high level of oil absorption, poor drying properties, and extreme hydrophilicity. Larger particle size is associated with more extreme phase separation and increased sensitivity to polar solvents. However, phase separation in the samples was linked to a reduction in the water sensitivity of the paint on aging. Reduced sensitivity to water in the impasto areas could be explained by the protective function of the skin of organic material of the hydrophilic pigment in relation to polar solvents.

Paints containing zinc oxide, anatase titanium dioxide, and ultramarine have been associated with water sensitivity in paintings (Tempest, 2009). Zinc oxide and ultramarine are hydrophilic and may facilitate the disruption of the surface of the paint during swabbing with aqueous solvents. A separate mechanism in which oil paint films become more accessible to polar solvents on aging may involve the breakdown of stearate additives, perhaps in synergy with other hydrophilic components.

Paints incorporating chromium oxide green on canvas without additives or with aluminum stearate had negligible sensitivity to aqueous solvents (–, +), whereas a higher sensitivity to saliva was observed when mixed with aluminum hydroxides (+), LF (2% and 5%), and HC (only at 10%; ++). Combinations of 10% metal stearates and 10% aluminum hydroxide resulted in a lower water sensitivity (–). Raw sienna paints on canvas were not affected by polar solvents (–), whereas samples on Melinex showed slight sensitivity to saliva (+) after aging.

The swab tests showed varying interactions with the paint surfaces that seemed to be generally related to the hydrophilicity or hydrophobicity of the surface. Chrome green and ultramarine paints with high oil content, especially on Melinex supports, were relatively unaffected by swabbing. Paints containing high percentages of added stearates were at first resistant to swabbing with any solvent and would suddenly break up and yield pigment from the underlying paint that remained vulnerable and was not fully cross-linked.

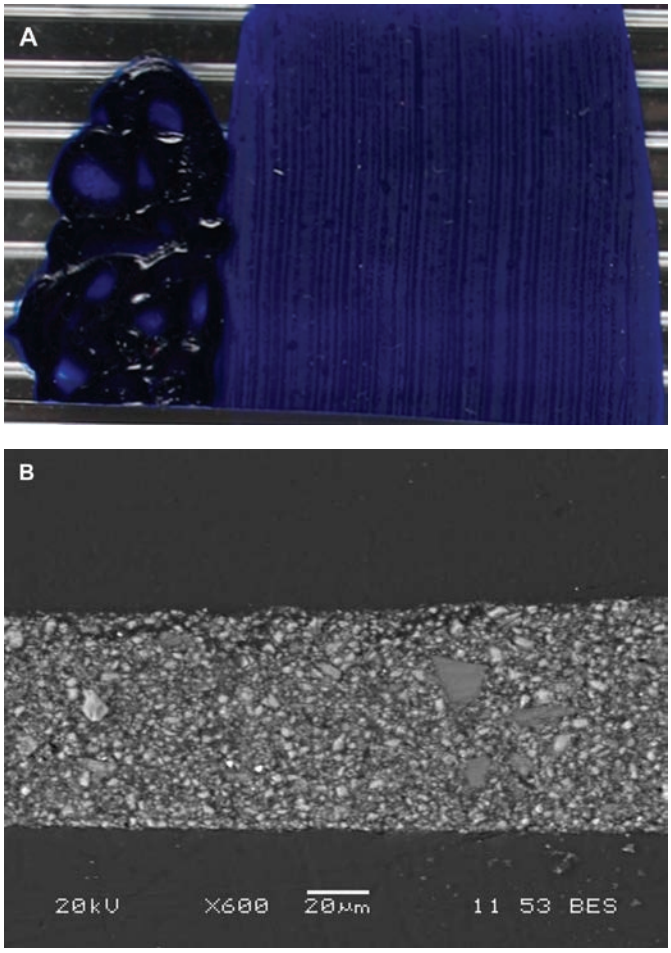


FIGURE 2. (A) Ultramarine 244 + 10% aluminum hydroxide, showing streaky surface appearance and slumped, glossy impasto. (B) Back scattered electron image of cross section of ultramarine 244 + 10% aluminum hydroxide, showing a paint-medium skin below the top layer of pigment particles.

The method for assessing the sensitivity of the paints did not account for the extreme behavior of the ultramarine-containing paint films; however, there was a close similarity to the reported behavior of ultramarine paints in paintings undergoing surface cleaning in previous studies (Wijnberg et al., 2007). The effect of excess stearate addition, linked with the formation of an incompletely cross-linked skin of medium and possibly the retardation of cross-linking of the underlying paint, produced the anomalous results in water sensitivity tests in this study. Further analysis is required to confirm this observation and to examine the skin of the medium in more significantly aged samples, which could present more oxidized or hydrolyzed surfaces and therefore be more hydrophilic. Degradation of the stearate additives may play an important role in the distinctive behavior of metal stearate–containing paint as it ages since this process will result in free fatty acids and aluminum hydroxide, which is hydrophilic. This effect may be particularly pronounced in films with a high oil content (such as ultramarine paints). The pH of the paint may also play a role, where the alkaline character of some films favors the formation of water-soluble soaps from free fatty acids or liberated by hydrolysis.

Test Paint Films: Surface Phenomena

Efflorescence was observed shortly after swabbing with aqueous solvents on the surface of water-sensitive chromium oxide green and ultramarine paints containing aluminum stearate on Melinex (Figure 3). It increased in density with increasing stearate content. Elemental aluminum remained distributed within the paint film, and FTIR of the bulk paint confirmed the presence of aluminum stearate (Figure 4). Although no increase in sensitivity was observed with additions of aluminum stearate in raw sienna paints, similar localized efflorescence was visible on samples on Melinex. The FTIR spectra for efflorescence on a variety of samples containing different pigments are characteristic of long-chain carboxylic acid (Figure 5). The SEM imaging shows planar, shardlike crystalline surface features that are present in abundance in areas of efflorescence and are absent, or

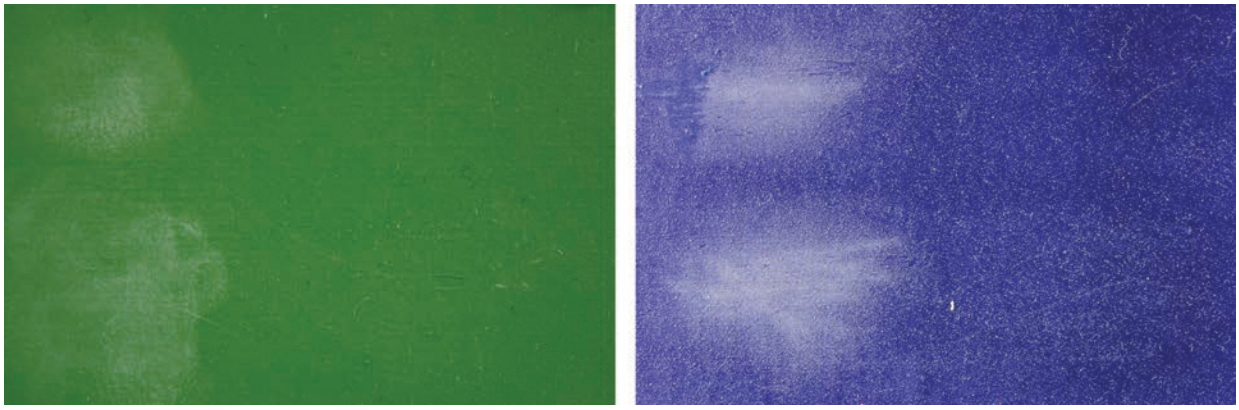


FIGURE 3. Localized efflorescence on (left) chromium oxide green + 20% aluminum stearate and (right) Winsor & Newton Winton French ultramarine + 20% aluminum stearate.

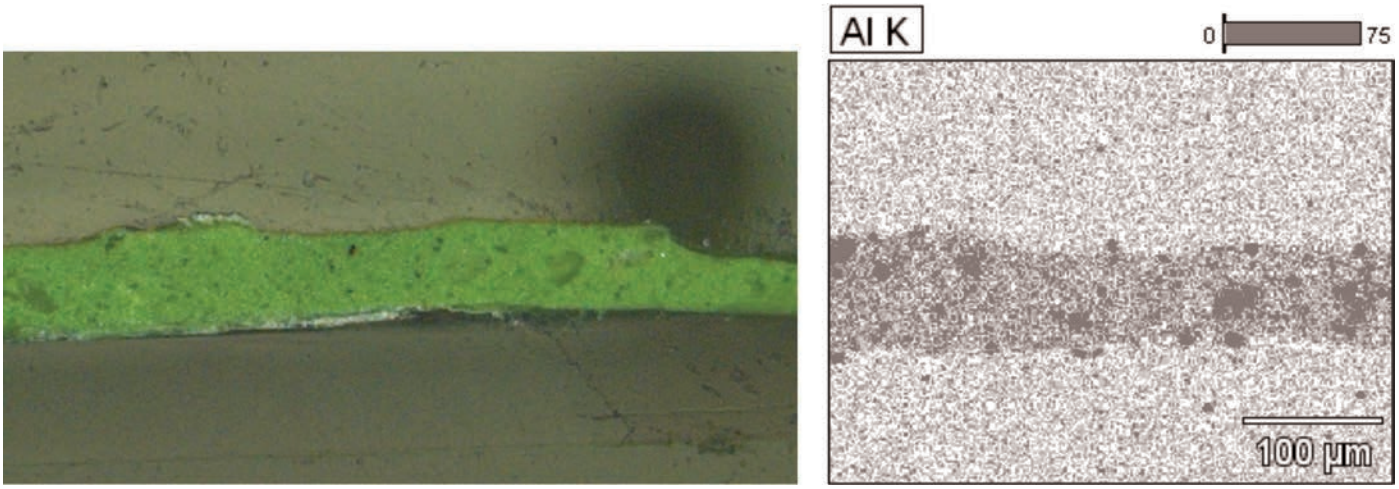


FIGURE 4. (left) Cross section of blanched area of chromium oxide green + 30% aluminum stearate on Melinex at ×100 and (right) Energy dispersive x-ray spectroscopy elemental mapping of the same area for aluminum, showing concentrations of elemental aluminum, which remained distributed in the paint film.

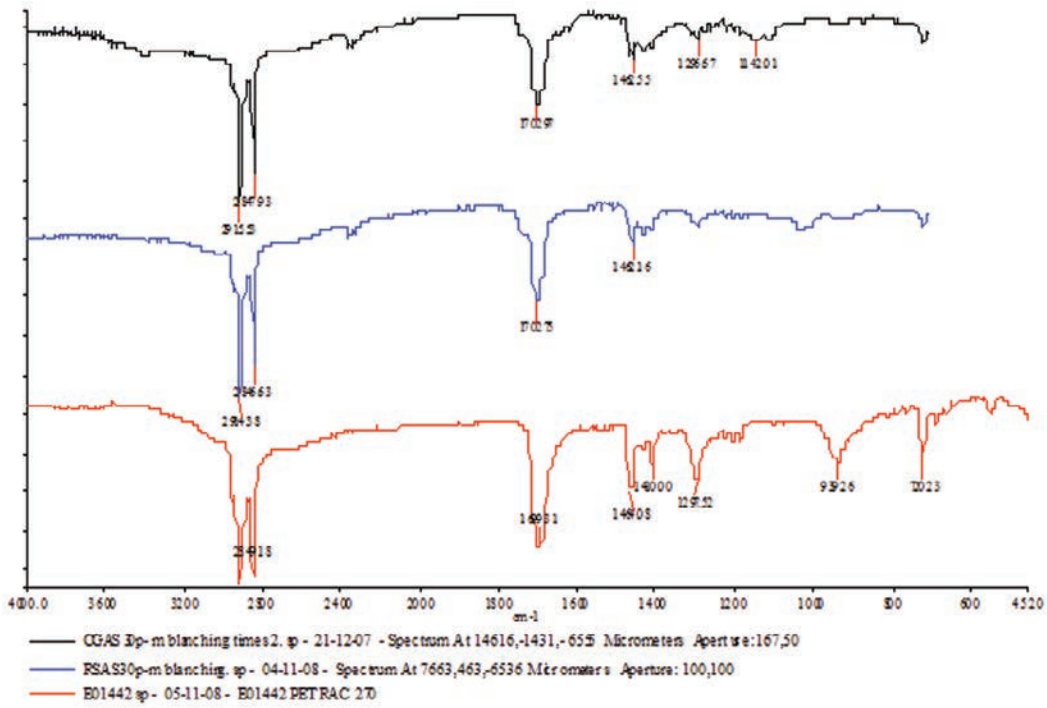


FIGURE 5. Fourier transform infrared spectra of scrapings of efflorescence on chromium oxide green + 30% aluminum stearate (CG; top line) and raw sienna +30% aluminum stearate (RS; middle line), both showing absorption bands, which are also present in the reference spectrum of stearic acid (E0; bottom line).

present only in low concentration, in areas where aqueous solvents have not been applied to the surface (Figure 6).

Other structures, distinct from fatty acid efflorescence, were observed using SEM on the surface of samples of water-sensitive oil paint films (Figure 7). The structures are visually similar to those containing magnesium and carbon observed by Mills et al. (2008) on the surface of Talens ultramarine, raw sienna, and cadmium yellow and red paint films (Figure 8). As there were no

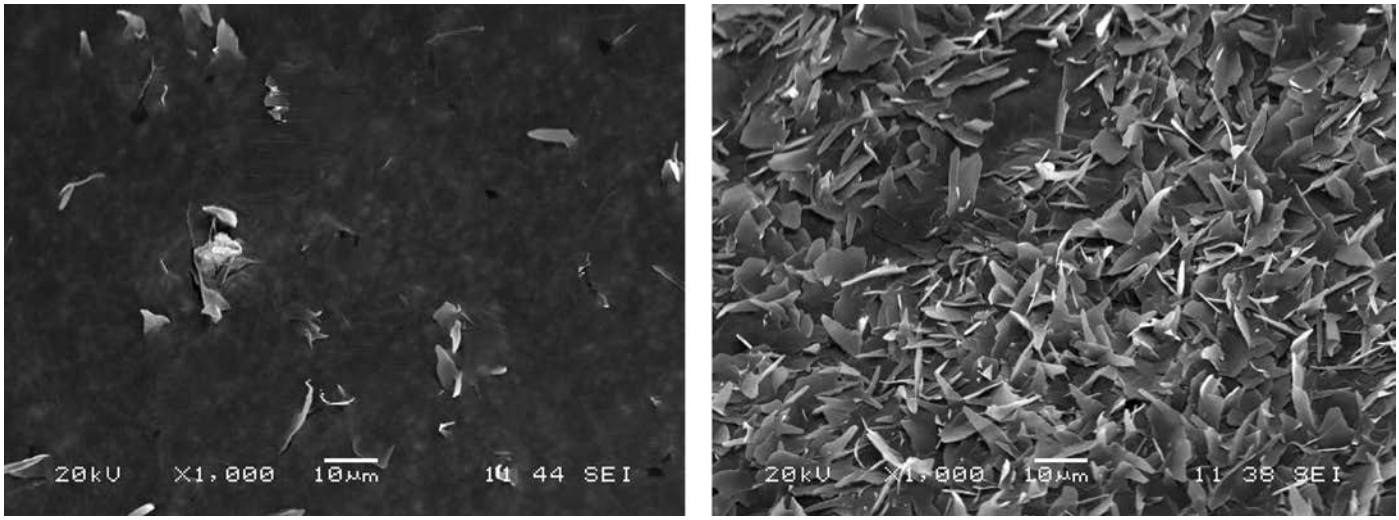


FIGURE 6. Secondary electron images (1000×) of (left) untreated aged paint surface and (right) localized stearic-acid efflorescence on Winsor & Newton Winton French ultramarine with 10% aluminum stearate added.

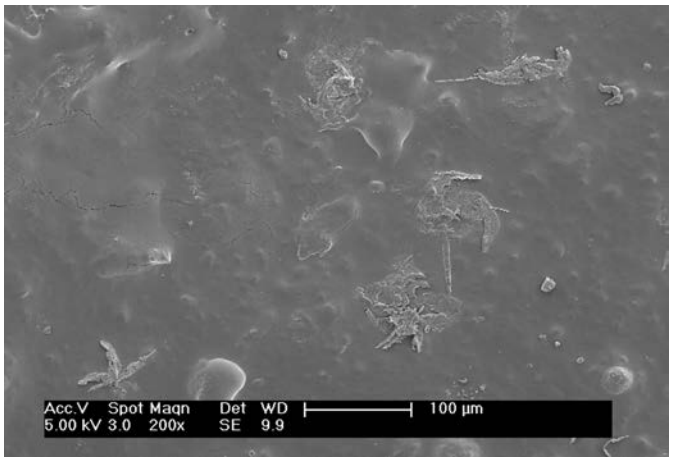


FIGURE 7. Scanning electron microscope image, 200×, of untreated aged surface of ultramarine 37 + 20% aluminum stearate on Melinex, showing clustered heterogeneous surface structures.

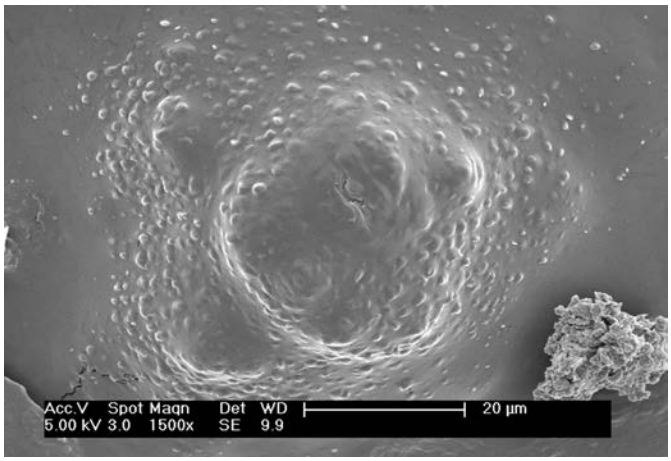


FIGURE 8. Scanning electron microscope image, 1500×, of untreated aged surface of ultramarine 37 + 10% aluminum stearate + 10% aluminum hydroxide on Melinex, showing lumpy, medium-rich protrusion.

magnesium-containing additives in the test paints, this indicates that some surface structures previously linked with degradation of certain additives, such as magnesium stearate or magnesium carbonate, can form in the absence of these additives.

CONCLUSIONS

Tests for water sensitivity by swab rolling after aging of linseed oil-bound test paint films indicated that additions of aluminum hydroxide and linseed oil fatty acids (also in combination with hydrogenated castor oil) enhanced the water sensitivity of the paints made using all pigments. Samples containing combinations of aluminum hydroxide and aluminum stearate generally reduced sensitivity to water. The evaluation criteria did not account for the phenomena observed in the ultramarine-containing paints with added stearates that formed a skin of medium at the surface that was initially resistant to swabbing with polar solvents. However, the paint beneath the skin was sensitive to polar solvents, and these samples responded to water in a manner very similar to that reported during the treatment of ultramarine passages in modern paintings.

It is proposed that metal stearates can both plasticize the paint and retard the drying process in oil-bound films. Free fatty acids, either as an integral additive (impurity associated with the metal stearates) or as a product of hydrolysis of the metal stearates, may migrate to the paint surface during drying or degradation of the film under normal environmental conditions, and in some films this process may be enhanced by cleaning treatments using water. Aluminum stearate–containing paints swabbed with aqueous solvents exhibited localized stearic acid efflorescence, whereas aluminum compounds remained distributed within the paint film. This may be associated with the breakdown of the metal stearates to form free fatty acids. The incorporation of aluminum hydroxide in addition to metal stearates appears to reduce both these tendencies, thus acting as a stabilizer.

The properties of pigments play a defining role in the characteristics of dried paint films and only certain combinations of pigment and additive result in water sensitivity. There is a relationship between the inclusion of metal stearates in oil paint and the occurrence of water and other solvent sensitivity. The presence of pigments that are poor driers, combined with the low pigment volume concentration enabled by the inclusion of metal stearates, can lead to a soft sticky film that may never fully polymerize, resulting in an open polymer network susceptible to swelling by polar solvents.

Future studies will look into the aging properties as well as the specific behavior of additives. Stearate (nondrying) fatty acids in cheap paints may turn into surfactants in alkaline environments. It is known that surfactants have been used in oil paint manufacture and are still used for lower-quality paints. Surfactants such as Duomeen, Empigen, and Empilan (P. Waldron and I. Garrett, Winsor & Newton, personal communication) may increase the water sensitivity. Furthermore, it has been suggested that bulking agents such as kaolin may increase solvent swelling in oil paint films, as demonstrated in acrylic paints (Ormsby et al., 2007). A relationship between swelling of oil paint films and the ionic strength of the cleaning solution has been proposed, and this relationship requires further exploration.

ANALYTICAL EQUIPMENT AND OPERATION CONDITIONS

The SEM-EDS analysis was undertaken using a JEOL JSM 5910 LV scanning electron microscope with a Noran Vantage EDS system with Pioneer Norvar detector as well as with a JEOL JSM-T100 SEM with INCA microanalysis suite 4.02. Imaging was done using a Philips XL30 with a field emission gun SEM and a LEO 1455 VP-SEM. Samples were coated with 20 nm of a gold-palladium alloy (80%:20%) using a Cressington sputter coater 208 HR. X-ray fluorescence spectrometry was performed at ICN using a Bruker Tracer III-V portable instrument, equipped with a low-power Rh tube operating at 40 kV and 2.2 μA and a Peltier cooled Si-PIN detector. X-ray-diffraction was performed on paint samples using a Platform GADDS microdiffractometer (Siemens-Bruker) with a HI-STAR Area Detector. The FTIR analysis was carried out using a Perkin Elmer Spectrum 1000 FT-IR spectrometer with Auto-image System FTIR Microscope and Diamond Anvil Cell and with a Perkin Elmer Spectrum 1000 FTIR combined with a Graseby Specac Golden Gate Single Reflection Diamond ATR.

Acknowledgments

We thank Shawn Digney-Peer, Phil Young, Roy Perry, Mariana Basto, Elisabeth Bracht, Louise Wijnberg, Laura Homer, Luuk van der Loeff, and Jay Krueger, modern paintings conservators, for sharing their experiences of treating water-sensitive oil paintings. We also thank Luc Megens and Ineke Joosten for SEM analysis at ICN, Suzan de Groot for FTIR analysis, Beatriz Verissimo Mendes and Alexia Soldano for sensitivity tests, and Wim van der Zwan and Steve Mills, Old Holland, for providing raw materials and an automatic muller for creating the test paints. We are grateful to Ian Garrett and Peter Waldron Winsor & Newton; Michael Harding; Dave Masterman, Holliday Pigments; Ian Maginnis; Juan Somoza, Nubiola Pigments; and Eva Eis, Kremer Pigmente for sharing their expertise about pigments and the paint-manufacturing process. Finally, we thank Alex Ball and Lauren Howard, Natural History Museum, London, for SEM imaging and Bill Luckhurst, King's College London, for SEM-EDS.

REFERENCES

Burnstock, A., K. J. van den Berg, S. de Groot, and L. Wijnberg. 2007. "An Investigation of Water Sensitive Oil Paints in Twentieth-Century Paintings." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. W. Krueger, and M.R. Schilling, pp. 177–188. Los Angeles: Getty Conservation Institute.

Gayler, S., A. Burnstock, and A. Vasconcelos. 2008. A Technical Study of Seminal Paintings from the 1960s by Robyn Denny in the Modern British Collection at the Gulbenkian Foundation, Lisbon. *Zeitschrift für Kunsttechnologie and Konservierung*, 22(1):63–72.

Mills, L. 2008. Water-Sensitive Oil Paints: An Experimental Investigation Characterising the Causes of the Phenomena and Analysis of a Case Study Painting *Les Animaux*, 1961, by Karel Appel. Student research project, Courtauld Institute of Art, London.

Mills, L., A. Burnstock, S. de Groot, L. Megens, M. Bisschoff, H. van Keulen, F. Duarte, and K. J. van den Berg. 2008. "Water Sensitivity of Modern Artists' Oil Paints." In *Preprints ICOM-CC 15th Triennial Meeting*, Volume 2, ed. J. Bridgland, pp. 651–659. New Delhi: Allied Publishers.

Ormsby, B., T. Learner, G. M. Foster, J. R. Druzik, and M. R. Schilling. 2007. "Wet Cleaning Acrylic Emulsion Paint Films: An Evaluation of Physical, Chemical and Optical Changes." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. W. Krueger, and M. R. Schilling, pp. 189–200. Los Angeles: Getty Conservation Institute.

Tempest, H. 2009. Water-Sensitive Oil Paint: An Experimental Investigation, with Case Studies and Survey, Further Characterising the Causes of the Phenomenon. Student research project report, Courtauld Institute of Art, London.

Tumosa, C. S. 2001. A Brief History of Aluminum Stearate as a Component of Paint. *WAAC Newsletter*, 23(3). http://cool.conservation-us.org/waac/wn/wn23/wn23-3/ (accessed 12 November 2012).

Wijnberg, L., K. J. van den Berg, A. Burnstock, and E. Froment. 2007. Jasper Johns' Untitled 1964 –'65. *Art Matters: Netherlands Technical Studies in Art*, 4:68–80.

Extended Abstract—The Effect of Conductivity on Water Solubility: Cleaning a Modern Chinese Oil Painting

Gillian Osmond and Anne Carter

INTRODUCTION

In preparation for the 2009 exhibition The China Project (Queensland Art Gallery, Brisbane, Australia), Wang Youshen's 1986 painting *Yu Gong and His Later Generations* was cleaned. Wang graduated in 1988 from the Folk Art Department of the Central Academy of Fine Arts, Beijing, majoring in illustration and graphic art. Wang's practice was formed during the New Wave period (1985–1989) in China, and he was included in the seminal 1989 exhibition China/Avant-garde held in Beijing.

The Queensland Art Gallery's painting is a rare early student work on hardboard. It is unvarnished, well bound, and of variable gloss (Figure 1, left). The paint film is generally stable; however, there are areas of yellow paint that are actively flaking. The painting was very dirty. Solubility testing showed that dirt was best removed using aqueous solutions but that all colors were sensitive in deionized water, particularly red paint.

MATERIALS AND ANALYSIS

The artist recalled using oil paint made locally in China (Tianjin) in the 1980s but could not remember the brand name. He did not use varnish but described mixing locally manufactured "megilp" with the oil paint (Summer Sun, ShanghART, and Wang Youshen, personal communication, 11 March 2010). Ultraviolet fluorescence imaging shows variable fluorescence, with pentimenti also visible as fluorescent underlayers (Figure 1, right).

Analysis using in situ X-ray fluorescence spectroscopy, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy of embedded cross sections, and Fourier transform infrared spectroscopy (FTIR) of paint samples revealed that zinc is widely present, predominantly as zinc stearate. Most paint layers contain similar inorganic material, including barium sulfate, silicates (kaolin and silica), chalk, and other earth elements. There are two distinct reds visible in cross section; they have different ultraviolet fluorescence properties and are distinguishable with backscatter electron imaging by the varying concentration of barium sulfate present. The FTIR analysis of two samples of red paint detected the presence of organic pigment PR3 (toluidine red) along with mixtures of drying oil and natural resin. The red sample with more barium sulfate also possibly contains wax but not zinc stearate.

***Gillian Osmond**, Centre for Contemporary Art Conservation, Queensland Art Gallery|Gallery of Modern Art, P.O. Box 3686, South Brisbane, Queensland 4101, Australia, and Australian Institute for Bioengineering and Nanotechnology, University of Queensland, St Lucia, Queensland 4072, Australia. **Anne Carter**, Centre for Contemporary Art Conservation, Queensland Art Gallery|Gallery of Modern Art, P.O. Box 3686, South Brisbane Queensland 4101, Australia. Correspondence: Gillian Osmond, gillian.osmond@qagoma.qld.gov.au; Anne Carter, anne.carter@qagoma.qld.gov.au.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

FIGURE 1. Wang Youshen (China, born 1964), *Yu Gong and His Later Generations* (Yu Gong he tade zizi sunsun), 1986. Oil on masonite, 94 × 79 cm. Courtesy of the Queensland Art Gallery; gift of Nicholas Jose and Claire Roberts through the Queensland Art Gallery Foundation 2008. (left) Photograph of the painting by Natasha Harth and (right) photograph of the ultraviolet fluorescence image by Gillian Osmond.

CLEANING

On the basis of information presented by Richard Wolbers during a cleaning workshop held at Queensland Art Gallery, Brisbane, in July 2008, surface conductivity and pH were measured across colors to inform design of a cleaning system. Wolbers recommends cleaning oil films with a solution in a pH range of 5.5–8.5 (one to two units above the surface measurement) and conductivity 10–20 times the surface readings. These parameters are to optimize soil removal without disrupting the paint surface. A solution with a suitable conductivity also aims to leave the paint surface electrically neutral and less likely to attract dust.

Measurements of the painting were taken before cleaning (Table 1). Both paint and dirt solubility were tested with water adjusted to pH 7.5 using triethanolamine, diluted to 1,000 µS/cm conductivity. The increased conductivity appeared to reduce the water sensitivity of the paint but required rinsing, which was not appropriate for the fragile surface.

Wolbers was consulted about ways to modify this cleaning system so it would not require rinsing. Phosphate was selected as a suitable buffer and ionic species. Sodium was recommended as the counter ion as it has a single positive charge and produces an inert complex with the cleaned oil surface (R. Wolbers, personal communication, 3 September 2008).

A solution of 0.05% dibasic sodium phosphate in deionized water was prepared. The pH was adjusted to 7.5 with hydrochloric acid. The solution was diluted to a conductivity of 1000 µS/cm and tested with good results. Areas previously considered too sensitive to clean with deionized water were able to be surface cleaned with no visible solubility issues. After cleaning, surface measurements showed a fairly consistent pH in the range 6–7, with conductivity readings indicating a reservoir of surface ions as planned (Table 1). In the future, monosodium phosphate will be used in preference to the dibasic form enabling pH to be adjusted with sodium hydroxide, thereby avoiding the presence of chloride ions.

CONCLUSIONS

The response of the painting to cleaning implies that its water sensitivity is at least partially related to ionic disruption of the paint. Deionized water acts as a hypotonic solution,

TABLE 1. Surface measurements carried out before and after cleaning. The areas measured are identified by paint color and location, i.e., BR = bottom right, CR= center right. Yellow paint was physically fragile and therefore was undercleaned, reflected in postcleaning readings; postcleaning measurements were avoided altogether in the second area of yellow paint.

	Red (BR)		Red (CR)		Yellow (BR)		Yellow (CR)	Green (BR)	
Measurement	**Before cleaning**	**After cleaning**	**Before cleaning**	**After cleaning**	**Before cleaning**	**After cleaning**	**before cleaning**	**Before cleaning**	**After cleaning**
Conductivity (μS/cm)	52	42	127	154	59	107	23	200	167
pH	7.1	6.4	5.5	6.2	6.6	5.7	5.3	6.4	6.6

extracting ions from the paint film to reach equilibrium, effectively solubilizing vulnerable paint. It is unclear if there is any connection to ongoing research by others investigating water sensitivity of modern oil paints attributable to phenomena such as hydrolysis of additives in the film (Mills et al., 2008).

Prior to this treatment, paintings were frequently cleaned with deionized water alone to avoid a rinsing stage. This case study demonstrates that customizing deionized water is a relatively simple way to reduce some potential impacts of surface cleaning, and this approach has now become routine practice.

Acknowledgments

The authors thank Richard Wolbers, University of Delaware, Bronwyn Ormsby, TATE, for the FTIR analysis undertaken, and John Drennan, Centre for Microscopy and Microanalysis, University of Queensland.

REFERENCE

Mills, L., A. Burnstock, F. Duarte, S. de Groot, L. Megens, M. Bisschoff, H. van Keulen, and K. J. van den Berg. 2008. "Water Sensitivity of Modern Artists' Oil Paints." In *Preprints ICOM-CC 15th Triennial Conference New Delhi*, pp. 651–659. New Delhi: Allied Publishers.

Extended Abstract—Noninvasive Assessments of Cleaning Tests on an Unvarnished Oil Painting on Canvas by Edvard Munch

Tine Frøysaker, Mirjam Liu, and Costanza Miliani

INTRODUCTION

Varnish is rare on the great majority of the paintings by Norwegian artist Edvard Munch (1863–1944). Empirical experience has shown that many of his oil colors are notably vulnerable to dirt removal, especially the lean blues, greens, yellows, reds, and whites (B. Topolova-Casadiego, The Munch Museum, personal communication, 5 March 2009). The removal of firmly attached dirt and dust (or any other impurities, e.g., tide lines from water stains or bird droppings) is and will continue to be utterly challenging for Munch's unvarnished paintings. This is particularly evident in paintings that are not protected by airtight, glassed frames, as is the case of *Chemistry*, one of the artist's 11 large-scale canvas paintings for the Aula of Oslo University (1914–1916).

For over 30 years, the surface of *Chemistry* (about 444 × 220 cm²) had been exposed to vast amounts of airborne pollutants, severely soiling it (Figure 1). In 2008, various aqueous and mechanical cleaning tests were performed. In order to evaluate the efficacy and harmfulness of each cleaning method with respect to the different colored areas of the painting, a noninvasive methodology based on in situ spectroscopic measurements, as well as visual examination, was carried out (Frøysaker et al., 2011).

MATERIALS AND METHODS

Eight colors (dark blue, blue mixed with white, dark green, green mixed with white, dark red, red mixed with white, semisolid paint on underdrawings of carbon black, and bare white ground) were selected for eight individual tests (about 2 × 2 cm in size). The locations were chosen on both exposed surface areas and on surfaces below the picture frame that have always been protected from light exposure and pollutants. The eight cleaning agents were (1) natural saliva, (2) Marlipal 1618/25, (3) Brij 700 gel (pH 6), (4) Triton X-100 gel (pH 8), (5) triammonium citrate (TAC) applied by cotton swab, (6) TAC applied by sponge, (7) vulcanized natural gum sponge, and (8) bread dough (Figure 2).

The surface examination was conducted by visual evaluation and optical microscopy (63×) and under UV lamp irradiation on the cleaned areas, on their surrounding colors, and on the cotton swabs used for application and cleansing. Then noninvasive measurements were carried out by mobile facilities for in-situ non-invasive measurements

Tine Frøysaker *and* ***Mirjam Liu****, Conservation Studies, Department of Archaeology, Conservation and History, University of Oslo, Frederiksgate 3, 0164 Oslo, Norway.* ***Costanza Miliani****, Consiglio Nazionaled delle Ricercha, Istituto di Scienze e Tecnologie Molecolari, Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto, 8, 06123 Perugia, Italy. Correspondence: Tine Frøysaker, tine.froysaker@iakh.uio.no; Mirjam Liu, mirjam.liu@gmail.no; Costanza Miliani, miliani@thch.unipg.it.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

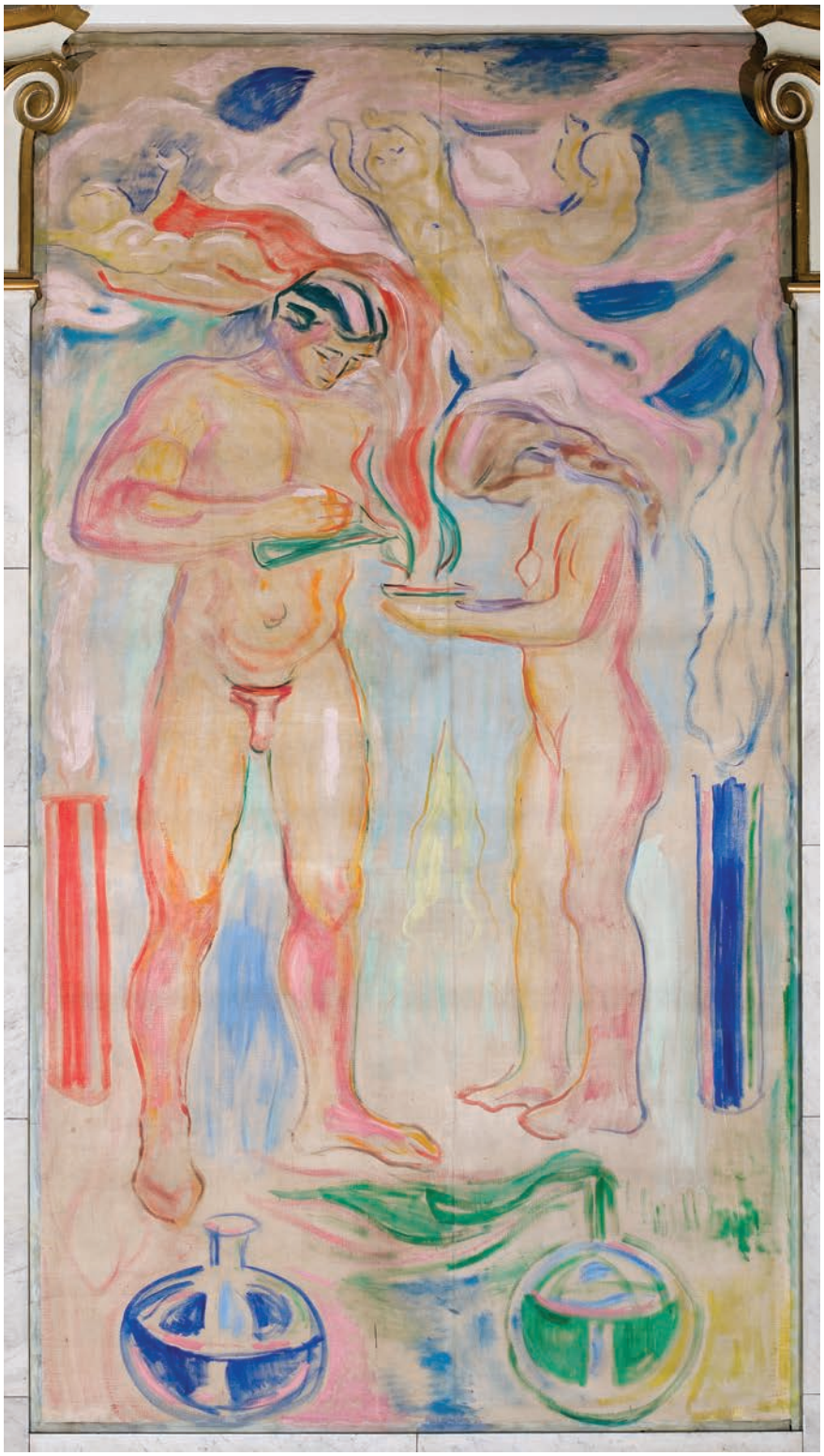


FIGURE 1. *Chemistry*. Unvarnished oil colors on white ground on canvas (1914–1916). About 440 × 220 cm^2. Photograph © Svein Andersen and Sissel de Jong, The Munch-museum/The Munch-Ellingsen-Group/BONO 2010.

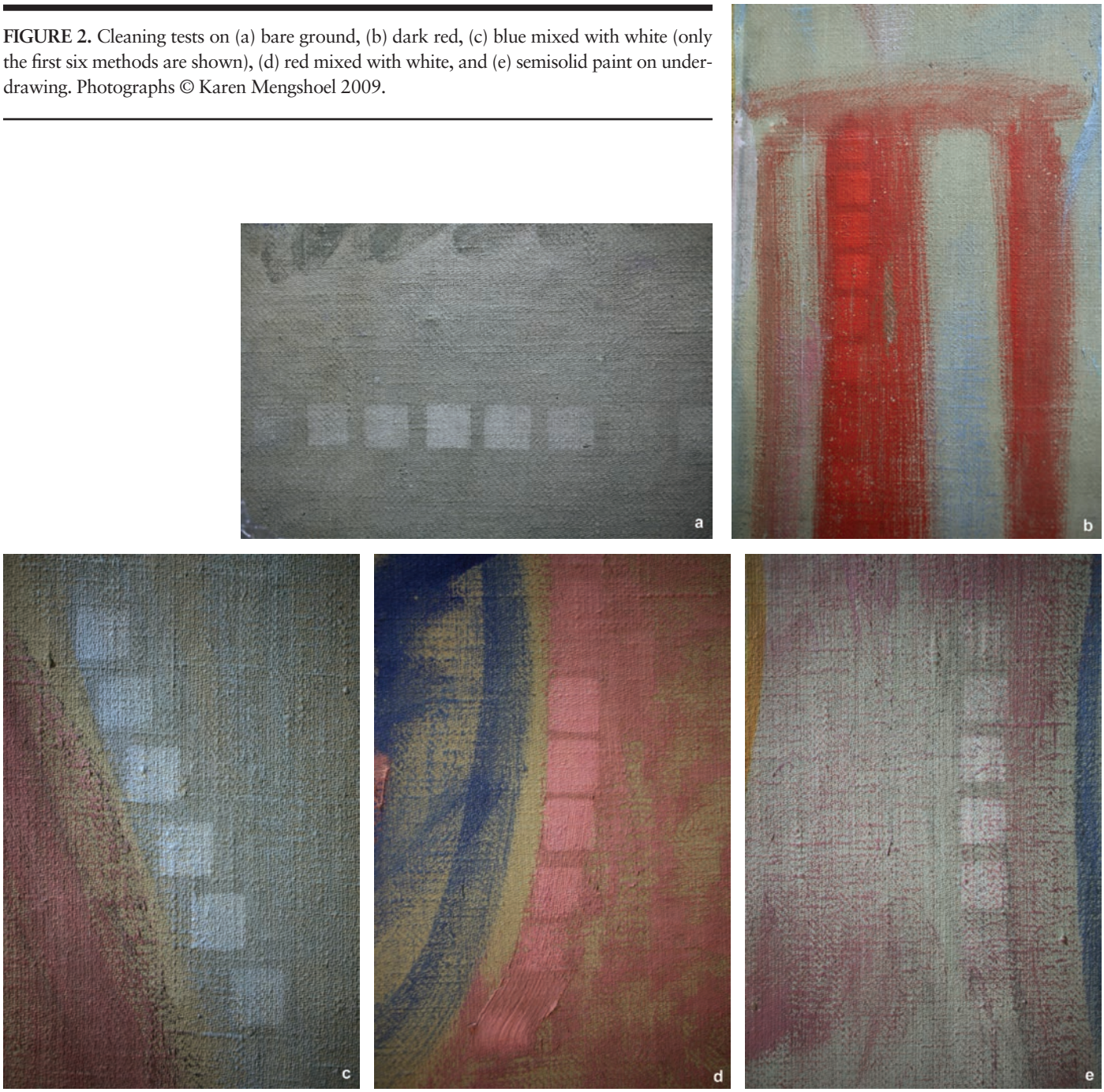


FIGURE 2. Cleaning tests on (a) bare ground, (b) dark red, (c) blue mixed with white (only the first six methods are shown), (d) red mixed with white, and (e) semisolid paint on underdrawing. Photographs © Karen Mengshoel 2009.

(MOLAB)'s mid-infrared Fourier transform infrared (FTIR) spectroscopy, resulting in some 130 spectra of the painting surface.

RESULTS AND DISCUSSION

The cleaning agents can be arranged according to the altered appearances of the test areas and the cotton swabs: natural gum could be used for all the colors tested, bread dough for six, Triton X-100 gel for five, TAC (applied by cotton swab) and Marlipal 1618/25 for four, natural saliva for three, and, finally, TAC (applied by sponge) and Brij 700 gel for two. Table 1 rates the first sets of 64 cleaning test on *Chemistry* by their visual appearance, microscopic examination (magnification 63×), and appearance under UV light.

The fiber-optic FTIR spectroscopy revealed various types of surface contaminants in uncleaned areas, such as sulfates, silicates, metal soaps (Pb and Zn), and zinc oxalates (Figure 3). The

TABLE 1. Results of the first sets of 64 cleaning tests on *Chemistry* as evaluated by visual inspection, by microcopic examination (magnification 63×), and under UV irradiation. For the evaluation numbers, a negative value indicates pigment loss: –6, uneven minimal cleaning; –5, even minimal cleaning; –4, uneven average cleaning; –3, even average cleaning; –2, uneven good cleaning; –1, even good cleaning. A positive value indicates no pigment loss: 1, uneven minimal cleaning; 2, even minimal cleaning; 3, uneven average cleaning; 4, even average cleaning; 5, uneven good cleaning; 6, even good cleaning.

	Color							
Test details	**Dark blue, diluted**	**Blue mixed with white**	**Dark green, diluted**	**Green mixed with white**	**Dark red, diluted**	**Red mixed with white**	**Semisolid paint on under-drawing**	**Bare ground**
Application area	laboratory flask below boy	back-ground behind girl	laboratory flask below girl	back-ground behind boy	test tube	cloud behind boy	girl's ankle	omnipresent
Pigments	ultra-marine, Prussian blue, cobalt blue	cobalt blue, emerald green plus white	emerald green, chrome green	emerald green, chrome green plus white	vermilion	vermilion plus white	vermilion plus white on carbon black	zinc white, lead white, chalk
Test 1, natural saliva	2	6	2	5	–4	3	1	1
Test 2, Marlipal 1618/25	–5	6	6	5	–3	6	4	3
Test 3, Brij 700 gel	–1	6	6	3	–1	3	–1	3
Test 4, Triton X-100 gel	–1	6	6	6	–1	6	–1	6
Test 5, triammonium citrate (cotton swab)	–5	6	6	6	–3	3	–1	6
Test 6, triammonium citrate (sponge)	–5	3	4	3	–3	6	1	1
Test 7, vulcanized natural gum sponge	2	2	2	2	2	2	2	2
Test 8, bread dough	2	2	6	3	4	2	2	3

first two were identified on the exposed areas and are responsible for the gray dust layer. The latter two are still invisible to the naked eye. The metal soaps were identified on both exposed and unexposed areas, but the zinc oxalates were only identified on the exposed surface and not below the frame.

When metal soaps become visible, they are seen as white surface deposits, and they are generally regarded as rather common in oil paintings from the 1600s to the early 1900s (van Loon, 2008). They form through the saponification of unsaturated fatty acids in either the binding medium and/or the ground layers. Their development is promoted by various factors, including high temperature and relative humidity (van Loon, 2008). They are removable by mechanical means or can be disguised by increasing their saturation with varnish. Saturation is, however, no option for the Munch Aula paintings since any kind of surface saturation will reveal the darkened canvas in all the areas of bare ground.

When visible, copper and calcium oxalates have been reported as either grayish brown surface crusts on easel paintings (Higgit and White, 2005) or as semiopaque film on murals (Nevin et al., 2008). They are highly insoluble and thus very difficult to remove by traditional methods. There is no known literature on the appearances of zinc oxalate salts or on their removal. If, or when, the zinc salts become visible on the Aula paintings (or any other paintings by Munch), they might cause radical changes to the appearances of the paintings and the artist's intent. Further research must be employed to delay the growth of possible visible and untreatable intrusions of the zinc oxalates on the paintings in question.

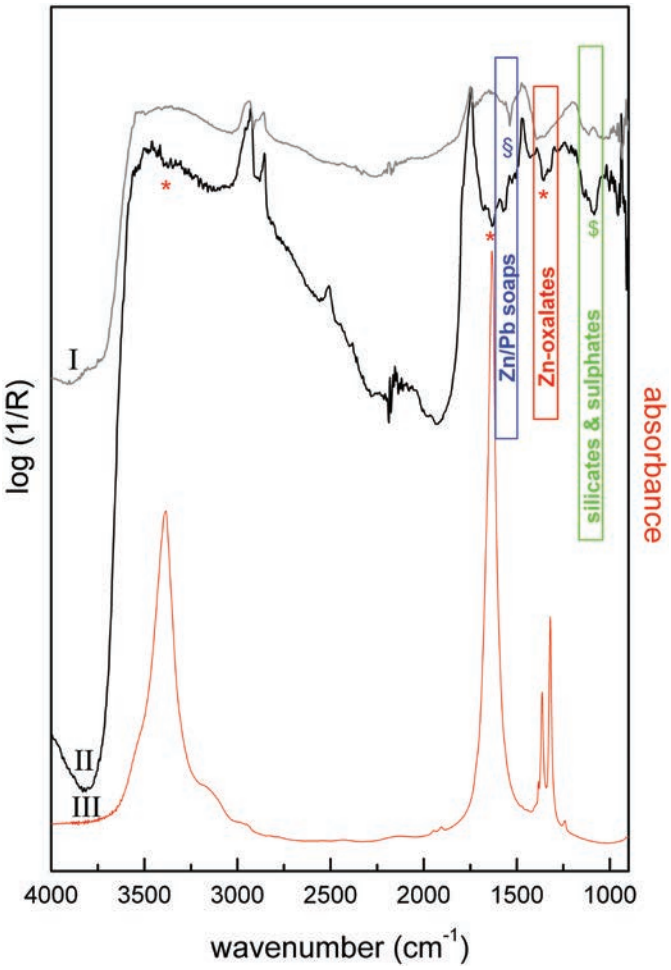


FIGURE 3. Noninvasive reflectance mid-infrared FTIR measurements: comparison of a spectrum collected on an uncleaned area (II, black line) with a spectrum of an area below the frame (I, gray line). The spectral region used for the identification of the different compounds is labeled: asterisk (*), diagnostic bands for Zn oxalates; section sign (§), diagnostic bands for Zn and Pb soaps, i.e., carboxylates; and dollar sign ($), diagnostic bands for silicates and sulfates. The transmittance of hydrated zinc oxalate is also shown (III, red line).

ACKNOWLEDGMENT

Access to the MOLAB was obtained thanks to the 6th Framework Programme (contract Eu-ARTECH, RII3-CT-2004-506171).

REFERENCES

Frøysaker, T., C. Miliani, and M. Liu. 2011. Non-invasive Evaluation of Cleaning Tests Performed on Chemistry (1909–1916). A Large and Unvarnished Oil Painting on Canvas by Edvard Munch. *Restauro*, 4:53–63.

Higgit C., and R. White. 2005. Analyses of Paint Media: New Studies on Italian Paintings of the Fifteenth and Sixteenth Centuries. *National Gallery Technical Bulletin*, 26:88–104.

Nevin, A., J. L. Melia, I. Osticioli, G. Gautier, and M. P. Colombini. 2008. The Identification of Copper Oxalates in a 16th Century Cypriot Exterior Wall Painting Using Micro FTIR, Micro Raman Spectroscopy and Gas Chromatography-Mass Spectrometry. *Journal of Cultural Heritage,* 9(2):154–161. http://dx.doi.org/10.1016/j.culher.2007.10.002.

van Loon, A. 2008. *Color Changes and Chemical Reactivity in Seventeenth-Century Oil Paintings*. MOLART Reports 14. Amsterdam: Netherlands Organization for Scientific Research.

Multitechnique Approach to Evaluate Cleaning Treatments for Acrylic and Polyvinyl Acetate Paints

María Teresa Doménech-Carbó, Miguel F. Silva, Elvira Aura-Castro, Antonio Doménech-Carbó, Laura Fuster-López, Jose V. Gimeno-Adelantado, Stephan U. Kröner, María Luisa Martínez-Bazán, Xavier Más-Barberá, Marion F. Mecklenburg, Laura Osete-Cortina, and Dolores J. Yusá-Marco

María Teresa Doménech-Carbó, Miguel F. Silva, Elvira Aura-Castro, Laura Fuster-López, Stephan U. Kröner, María Luisa Martínez-Bazán, Xavier Más-Barberá, Laura Osete-Cortina, *and* ***Dolores J. Yusá-Marco****, Instituto de Restauración del Patrimonio, Universidad Politécnica de Valencia, Camino de Vera s/n, 46022 Valencia, Spain.* ***Jose V. Gimeno-Adelantado*** *and* ***Antonio Doménech-Carbó****, Departamento Química Analítica, Universitat de Valencia, Estudi General, Avenida Doctor Moliner s/n, 46100 Burjassot, Spain.* ***Marion F. Mecklenburg****, Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Road, Suitland, Maryland 20746-2863, USA. Correspondence: Maria Teresa Doménech-Carbó, tdomenec@crbc.upv.es; Miguel F. Silva, midesou1@gmail.com, Elvira Aura-Castro, eaura@crbc.upv.es; Laura Fuster-López, laufuslo@crbc.upv.es; Stephan U. Kröner, ustephan@upvnet.upv.es; María Luisa Martínez-Bazán, lmartine@crbc.upv.es; Xavier Más-Barberá, jamasbar@bbaa.upv.es; Laura Osete-Cortina, losete@crbc.upv.es; Dolores Julia Yusá-Marco, doyumar@crbc.upv.es; Jose V. Gimeno-Adelantado, jose.v.gimeno@uv.es; Antonio Doménech-Carbó, antonio.domenech@uv.es; Marion F. Mecklenburg, mecklenburgm@si.edu.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

ABSTRACT. A multitechnique approach was applied to two types of commercial paints, Liquitex (acrylic) and Flashe (polyvinyl acetate) to evaluate cleaning treatments carried out with water and a selection of organic solvents having different polarities. The analysis included weight loss and water absorption-desorption tests; pyrolysis–gas chromatography–mass spectrometry, Fourier transform infrared spectroscopy, UV-Vis spectrophotometry, light microscopy, scanning electron microscopy, atomic force microscopy, voltammetry of microparticles, mechanical tests, and microtensile tests. The study showed, among other results, differences in the mechanical behavior of both types of paints after exposure to water and other organic solvents. These differences correlate well with content changes of additives and pigments after cleaning. Morphological changes after cleaning can also be correlated with compositional changes in the film depending on the solvent used.

INTRODUCTION

Until some years ago, conservation treatments aimed to solve the problems presented by centuries-old paintings. These depended on the polymerization, cross-linking, and/or hydrolysis reactions that the paint might have experienced, the films' drying times, and the internal stresses that could have developed within the painting structure as a consequence of the many intrinsic and extrinsic variables that could have changed over the years.

The industrial development during the twentieth century led to the progressive development of synthetic media and paints. Because of the complexity of these products, whose composition and formulation are not known, the interactions of pigments, media, and all kind of "enhancers" in the behavior of the resulting films have yet to be characterized as these will affect their aging characteristics and stability over time.

Presently, the problems presented by the conservation of modern and contemporary paintings make essential the knowledge of these synthetic formulations. The lack of the time perspective makes understanding how polyvinyl acetate (PVAc) and acrylic paint films form, what determines their stability, and how they interact with both the environment and the materials and methods used by conservators crucial for the development of appropriate conservation treatments.

The study of the effects of cleaning treatments on the physical and chemical properties of artists' materials has increasingly attracted the attention of researchers in the field of conservation science since the 1990 IIC Brussels Congress "Cleaning, Retouching and Coatings" (Mills and Smith, 1990). In particular, a significant number of papers focus on the effects of cleaning of modern materials such as acrylic media (Ormsby and Learner, 2009).

Alternative cleaning methods to swabbing (with water, pure solvents, or their mixtures to obtain specific polarities) include the use of gels, emulsions, surfactants, and chelating agents, among others, which apart from their low toxicity, aim to minimize the penetration and retention action of solvents as well as to control their effectiveness. This is particularly true for the case of gels and emulsions.

Gels are helpful in avoiding the rapid penetration of water and solvents into the paint layers.

Emulsions allow the formulation of stable cleaning mixtures from nonmiscible solvents by adding a surfactant as an emulsifier. In particular, water-in-oil emulsions allow water to be in contact with water-sensitive surfaces that cannot be exposed directly to it. This is helpful in the case of waterborne acrylic and PVAc paints. The resulting emulsion mixture can then be applied with a brush, bringing the micro-particles of emulsified water in contact with the surface of the acrylic film. Finally, surfactants and chelating agents can be designed to act selectively on specific materials that need to be removed.

A multitechnique approach to evaluate different cleaning methodologies was applied to a selection of both acrylic and PVAc paints in an attempt to provide practical understanding of the effects of cleaning with water and solvents and therefore the consequences that a conservation treatment might have on an artwork. Insights into the following questions, among others, were sought:

- How are these paints affected by water and/or solvents?
- To what extent does the application methodology significantly influence the resulting action of water and/or solvents (in terms of both effectiveness and potential damage risks)?
- Are gels and emulsions a valid solution in terms of effectiveness and limitation of risks associated with retention and residue issues?

EXPERIMENTAL METHODS

Commercial PVAc and Acrylic Paints

The PVAc paints tested were Flashe paints (supplied by Lefranc & Bourgeois). The colors studied included oriental red, green armour, Senegal yellow, and burnt umber. The acrylic paints tested were Liquitex (Heavy Body) phthalocyanine blue, red oxide, Hansa yellow, cadmium yellow, Mars yellow, burnt umber, raw umber, titanium white, naphthol red, and Liquitex gloss medium and varnish. Talens Studio raw sienna, Talens glossy medium, and Talens gel medium were also tested.

Preparation of Test Specimens

Film specimens were prepared by casting the paints onto Mylar sheets and allowing them to dry for 1 to 2 years before testing. The resulting films exhibited an average thickness of 0.15 mm.

Immersion Tests

Samples weighing approximately 0.4–0.5 g were immersed in deionized water or solvent (ethanol, acetone, white spirit, or ligroin) for 10 minutes, 20 minutes, and 12 hours. In the case of pure binding media, such as Talens glossy medium and Talens gel medium, water immersion for 90 minutes was carried out. The films were then removed, dried from the excess of water or solvent, weighed, and analyzed. An aliquot of the resulting liquid extract was preserved, and another aliquot was dried at 50°C in a laboratory oven and then analyzed.

Gel and Emulsion Cleaning Methods

Vanzan gel (a xanthan gum with a high molecular weight water-soluble polysaccharide thickener) was prepared by mixing 1 g of Vanzan in 50 mL of deionized water.

Klucel G gel (a nonionic cellulose ether) was prepared by mixing 2g of Klucel G in 50 mL of deionized water.

A ligroin in water (water in oil, W/O) emulsion was prepared by first mixing 10 mL of water with 4 mL of Brij 30 (a nonionic polyoxyethylene surfactant) and then adding 90 mL of ligroin. Both gels and emulsions were applied by brushing. After a specified time, they were removed with a dry cotton swabs, and then the surface was swabbed with water.

Instrumentation

The analytical techniques applied are the following; the working conditions for the instruments and procedures for sample preparation were similar to those of previous studies: (1) weight measurements of water absorption-desorption and weight loss tests performed with a Precisa XT 120-A precision balance, (2) pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS; Osete-Cortina and Doménech-Carbó, 2006; Silva et al., 2010), (3) Fourier transform infrared spectroscopy and UV-Vis spectrophotometry (Doménech-Carbó et al., 2006b:156), (4) light microscopy (Doménech-Carbó et al., 2006a:162), (5) scanning electron microscopy (SEM) and atomic force microscopy (AFM; Doménech-Carbó et al., 2006b:156), and (6) mechanical tests and microtensile tests (Silva et al., 2010). Mechanical and microtensile tests were carried out on the films after they had been dried for 1 month at laboratory conditions (23°C and 55% RH) after treatment.

RESULTS AND DISCUSSION

Water Immersion of Test Films

Waterborne acrylic and vinyl paints are not soluble in water but are highly sensitive to liquid water. The sensitivity of these products has been tentatively attributed to the presence of additives included in the paint formulations (Juhué and Lang, 1993; Kientz and Hall, 1993; Juhué et al., 1995; Belaroui et al., 2003).

Figure 1 shows the water absorption curves obtained by a 20 minute immersion of Liquitex Heavy Body (HB) acrylic paint films in deionized water. The specimens tested (average thickness of 0.15mm) were nearly fully penetrated in this time, whereas they took about 2 to 4 hours to dry, although complete drying may require days. All colors exhibited weight loss due to the extraction of water-soluble additives present in the bulk film.

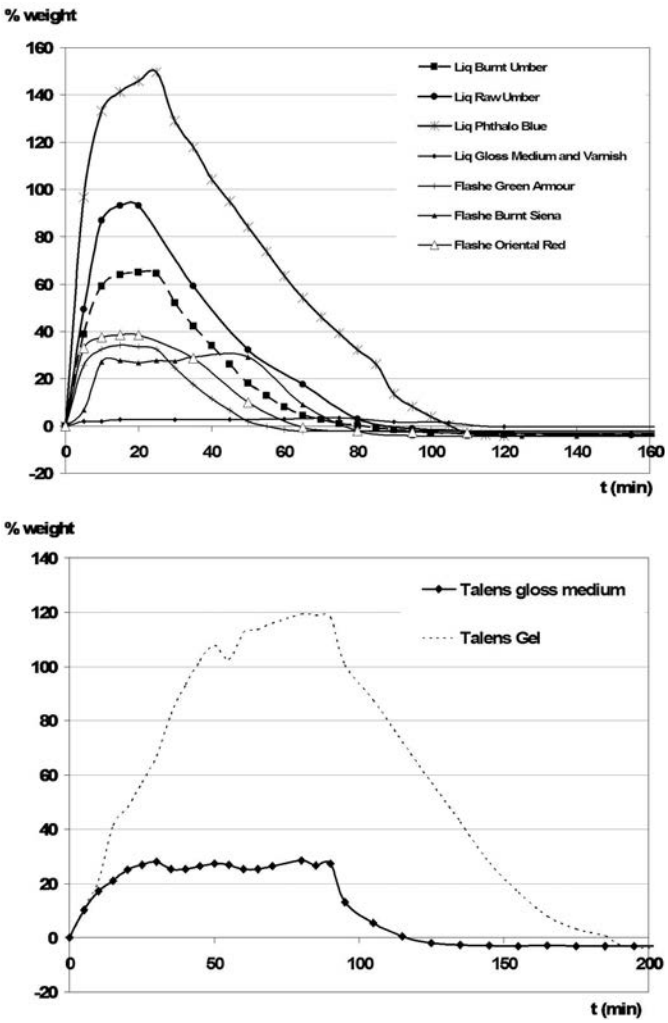


FIGURE 1. (top) Water absorption and drying curves for acrylic Liquitex Heavy Body and PVAc Flashe paint films (average thickness of 0.15 mm) after a 20 minute immersion of deionized water. Note that the acrylic paints phthalocyanine blue and naphthol red showed practically the same behavior, and this also occurred for the oriental red and the Senegal yellow. (bottom) Equivalent curves for the Talens gel and Talens gloss medium after 90 minute immersion.

The acrylic paints showed a variable water uptake, depending on their color, that ranged between 60% and 200% weight in the first 20 minutes of immersion. Interestingly, synthetic colors such as naphthol red and phthalocyanine blue exhibited the highest water absorption and visible swelling when compared to earth colors and other inorganic pigments. Likewise, the synthetic colors also exhibited more weight loss. This result indicates that the formulations are *tailored* by the manufacturers to stabilize the emulsion as a function of pigments and additives, which will clearly affect the overall water sensitivity of the dried film. In contrast, Liquitex acrylic medium and varnish films were unaffected by the water exposure during immersions, showing low weight gain and minimum swelling.

After a 90 minute immersion, Talens acrylic glossy medium and Talens gel medium showed extensive water absorption and swelling, and this behavior differs significantly from that of the Liquitex binding medium. The gel absorbed far more water than the glossy medium, indicating the presence of additives that affect the water sensitivity of the final product. The analysis of these products by Py-GC-MS revealed that both products, the glossy and the gel medium, are ethyl acrylate-methyl methacrylate-butyl acrylate polymers.

The PVAc Flashe paints contain a high pigment volume concentration and behave as brittle paints when compared to the acrylic paints described previously. The immersion tests performed for these paints (Figure 1) showed that most colors exhibited similar water absorption-drying profiles, with the exception of the earth colors. Most of the earth color films lost cohesion when subjected to the immersion tests, which is probably related to the expansion of the clay minerals in the film. The absorption-drying profile for burnt sienna and green armour reveal higher water retention after the immersion test that can be attributed to the presence of clay minerals from the earth pigment.

Effect of Water Immersion on the Mechanical Properties of Test Films

Figure 2 shows the stress-strain plots of the acrylic Liquitex HB burnt umber and phthalocyanine blue films after a series of water or solvent immersions. The curves for the burnt umber are representative for all acrylic and the PVAc Flashe paint films.

From these curves, it becomes evident that the effect of the immersion on the mechanical properties of the acrylic films requires some 20 minute immersions to become significant. This may be related to the fact that it took water this amount of time to fully penetrate into the film, promoting the leaching of additives and inducing changes in the lattice structure. Consequently, it can be considered that for a short exposure to water these films are almost unaffected.

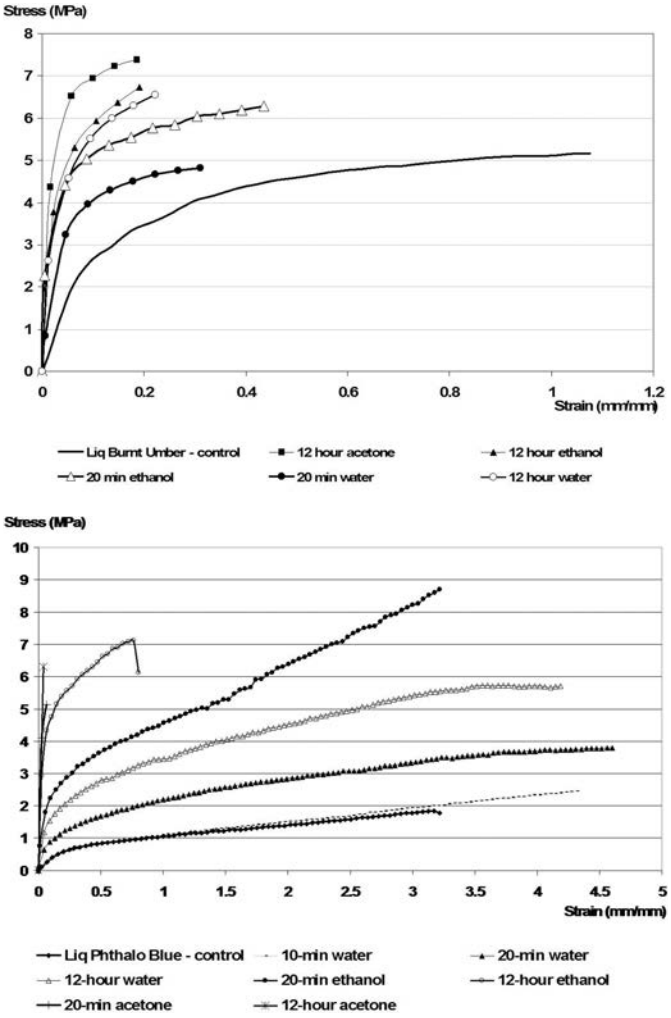


FIGURE 2. Stress-strain plots of (top) the acrylic Liquitex HB burnt umber paint film and (bottom) phthalocyanine blue paint film for the control test and after immersion in water or solvent for different times. The behavior of the burnt umber paint reflects that of the acrylic and PVAc paints in general.

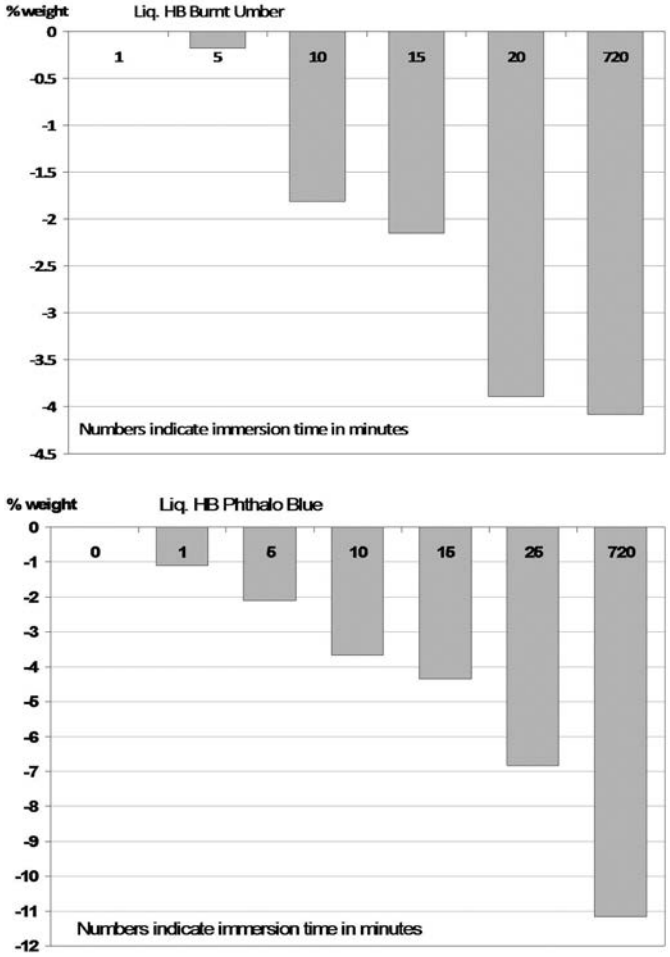


FIGURE 3. Weight loss as a function of water immersion time for the acrylic Liquitex HD (top) burnt umber and (bottom) phtalocyanine blue paint films.

All paint films tested, i.e., acrylic and PVAc, except for the phthalocyanine blue, showed an increase in stiffness and a decrease in the elongation-at-break values after 20 minute and longer immersion times in water, ethanol, or acetone. As shown in Figure 2, acetone dissolves the polymer chains much faster than ethanol, making the paint film far more brittle, as shown above for the 20 minute and 12 hour immersions in acetone. The 12 hour exposure to ethanol embrittles the paint film far more than the equivalent water immersion. Interestingly, the phthalocyanine blue films showed an increased plastic deformation capacity for the case of water.

Bar charts illustrating the weight loss for both these paints as a function of immersion time in water are shown in Figure 3. The extraction of minor compounds present in the bulk films can be readily measured in the first few minutes of immersion, particularly for the phthalocyanine blue, explaining the different mechanical properties of these films when exposed to water immersion longer than 20 minutes.

The examination of both acrylic and PVAc paints by SEM clearly showed that water immersion creates micropores in the structure of the film (Figure 4). Complementary data collected with a microtensile strength tester coupled to a light microscope showed that these micropores were the starting points for cracking of these films when subjected to stress.

Mechanical Properties of Acrylic Films after Water Immersion and Swabbing Tests

The mechanical properties of acrylic Talens raw sienna films were evaluated after 5 and 20 minute water swabbing or water

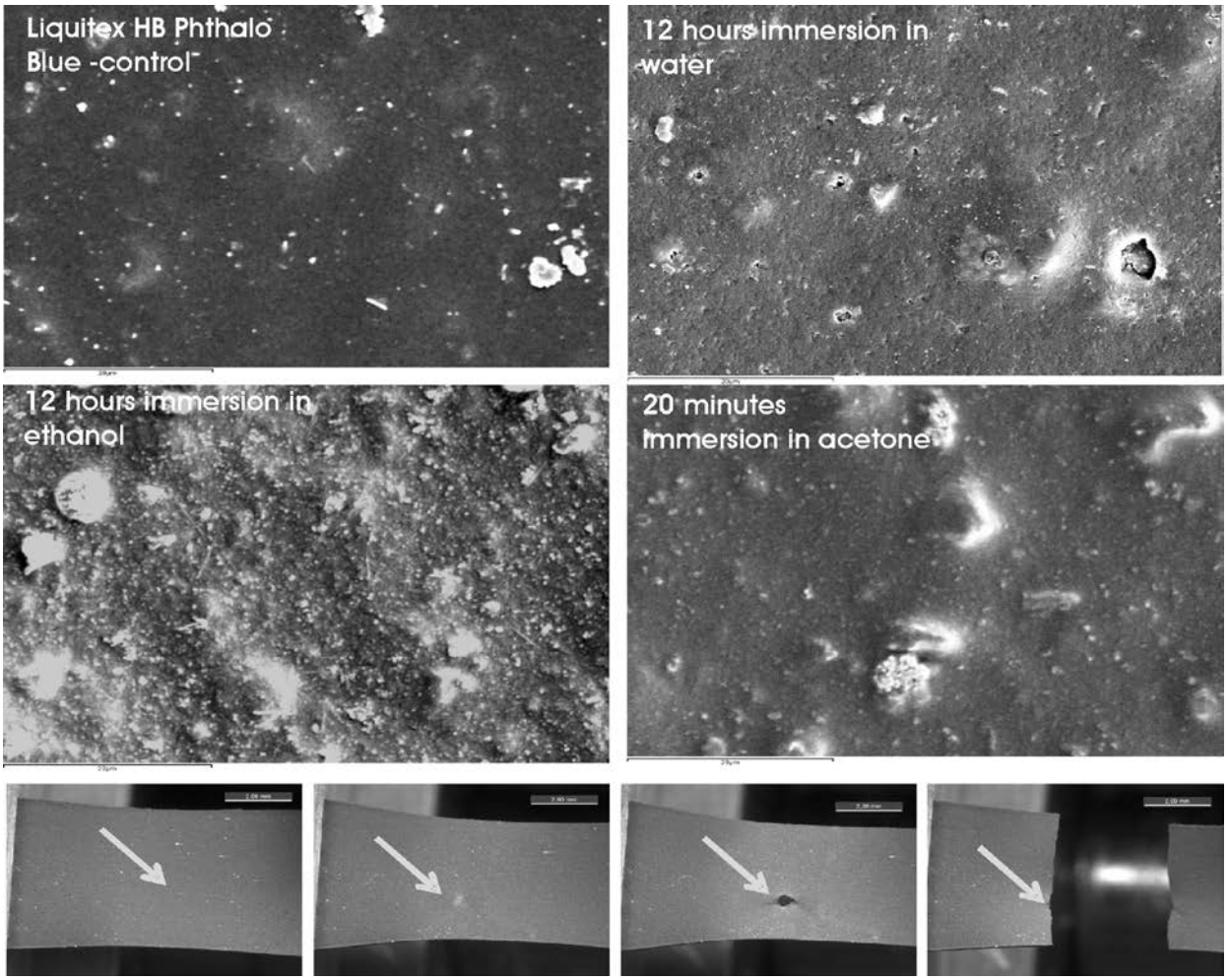


FIGURE 4. The SEM photomicrographs of acrylic Liquitex HB pthalocyanine blue films before and after immersion in water (12 hours), ethanol (12 hours), and acetone (20 minutes). The photos below show light microphotographs taken during microtensile testing, where the starting points for the mechanical failure are the micropores.

immersion tests. The stress-strain curves are presented in Figure 5 and show that these samples, similar to most acrylic ones, underwent an increase in stiffness and elongation-at-break values within 5 minutes for both immersion and swabbing. It is evident that in the first few minutes, the immersions affect the paint's mechanical properties more dramatically. However, after 20 minutes of water exposure, both immersion and swabbing present similar stress-strain curves, indicating that water swabbing for longer periods of time may have mechanical effects on paints similar to those obtained with water immersion.

Effect of Solvent Immersion on Test Films

In general, the exposure of acrylics and PVAc paints to solvents resulted in the dissolution of polymer chains and extraction of additives. The AFM images presented in Figure 6 show a PVAc Flashe Senegal yellow paint film before and after immersion in acetone. The exposure of these films to solvents with lower polarity than water, such as acetone and ethanol, resulted in an increase in the roughness of the surface at micro- and nanoscales as the grains of pigment become more evident. This shows not only that additives are being removed but also that large amounts of polymer chains are being extracted, which affects directly the overall properties of the films.

As mentioned, acetone affects the paint films by dissolving the polymer chains much faster than ethanol. As a consequence, the samples readily became stiff and brittle and almost impossible to test. Ethanol, on the other hand, affects the mechanical properties of the film in the first 20 minutes after immersion, but it takes a longer exposure time to embrittle the sample.

On the other hand, both acrylic and PVAc paints showed less susceptibility to nonpolar solvents such as ligroin and white

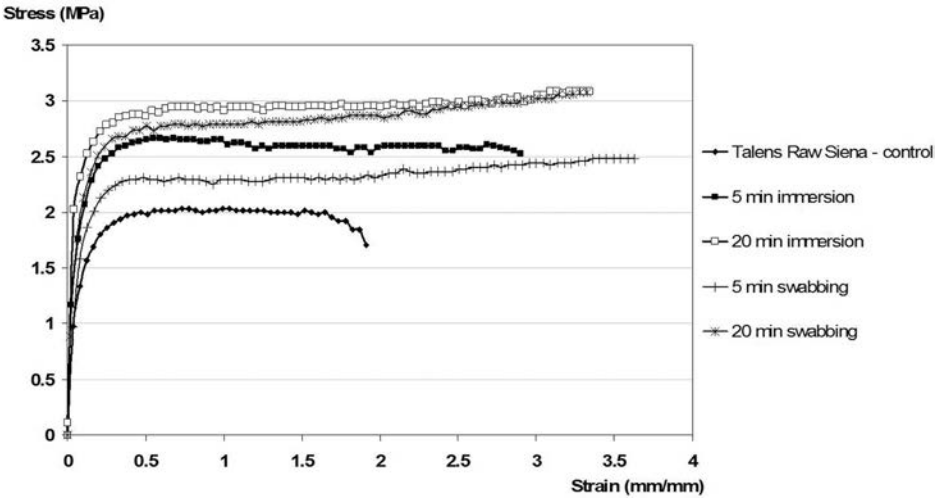


FIGURE 5. Mechanical properties for Talens raw sienna films after 5 and 20 minutes of water swabbing or immersion.

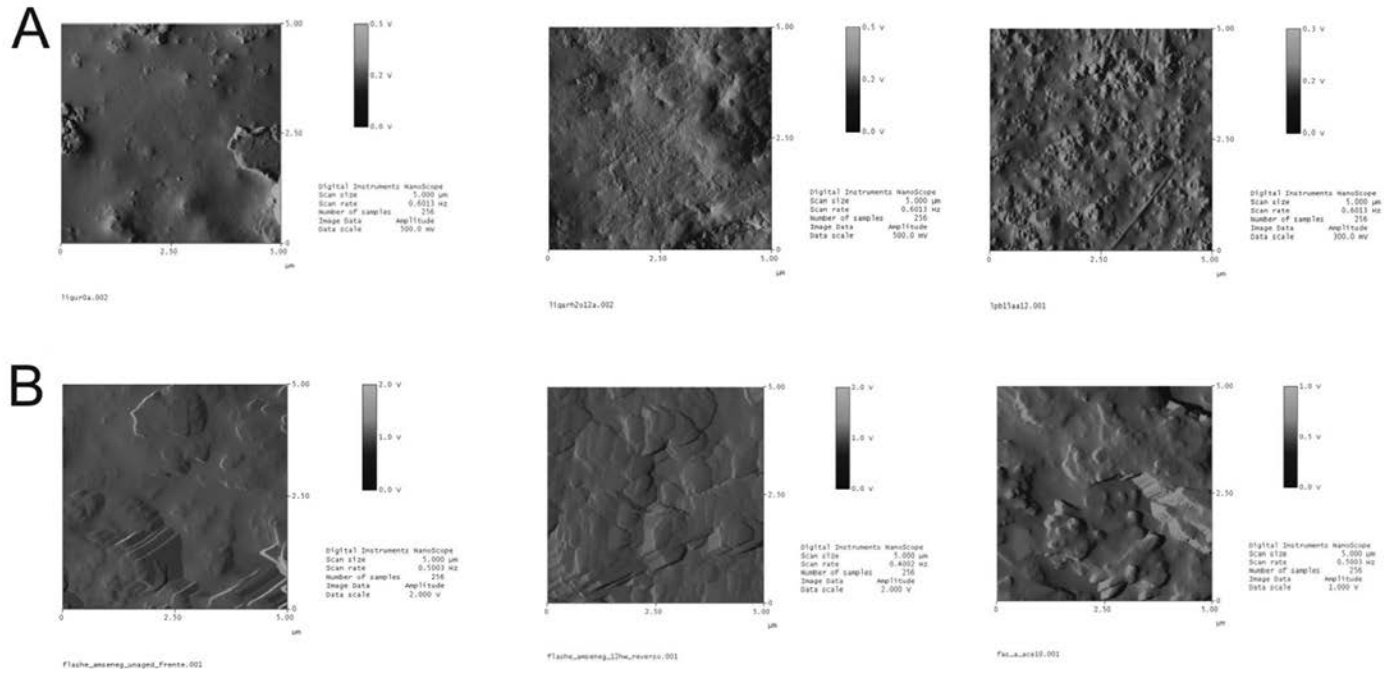
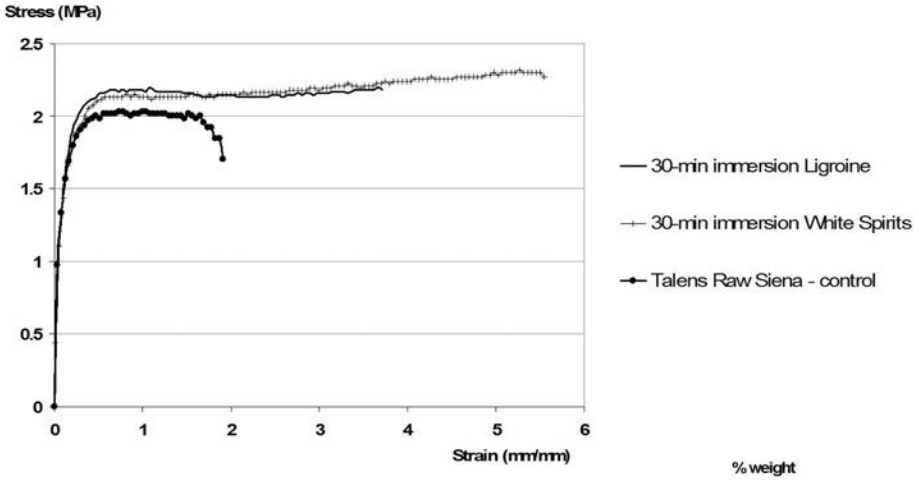


FIGURE 6. The AFM images of PVAc Flashe Senegal yellow paint film (A) before and (B) after immersion in acetone. (left) Unaged films, (middle) 12 hour water immersion, and (right) 20 minute acetone immersion.

spirit, as discussed in prior studies (Zumbühl et al., 2006). Aliphatic solvents did not produce an evident swelling effect in any of the paint films tested. Nevertheless, it was interesting to note that the samples retained these solvents for a long time, resulting in a plasticizing effect of the paint films, which is shown by an increase in the elongation-at-break values (Figure 7). It is important to mention that there was a slight increase in the stiffness of Talens raw sienna specimens after 30 minute immersion in either ligroin or white spirit. Furthermore, the SEM surface examination of the same test specimens, as well as those treated with water, revealed alterations in their micromorphology, including the appearance of microfissures visible at very high magnification (Figure 8).

Interestingly, the 12 hour water immersion of PVAc Talens raw sienna severely affected the paint film; the whitish aspect of the SEM image is due to the migration of calcite and clay minerals from the core to the surface of the film (Wedin and Bergström, 2005). This is likely related to the swelling of these particles with water and consequent migration in the water-swollen latex.



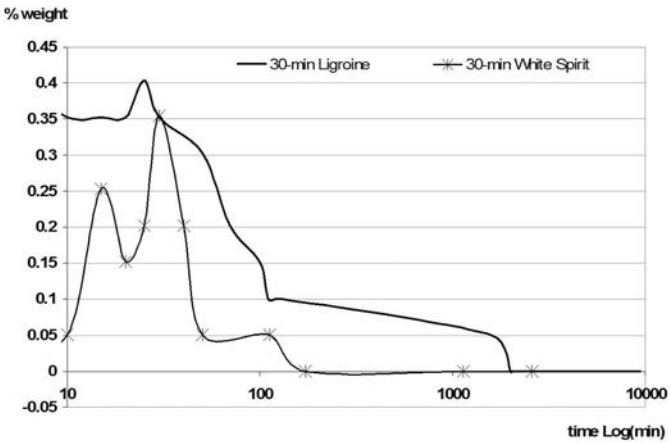


FIGURE 7. (top) Stress-strain plots for Talens raw sienna paint films before and after 30 minute immersion in either ligroin or white spirit. (bottom) Weight increase and loss for the samples during and after 30 minute immersion in white spirit or ligroin.

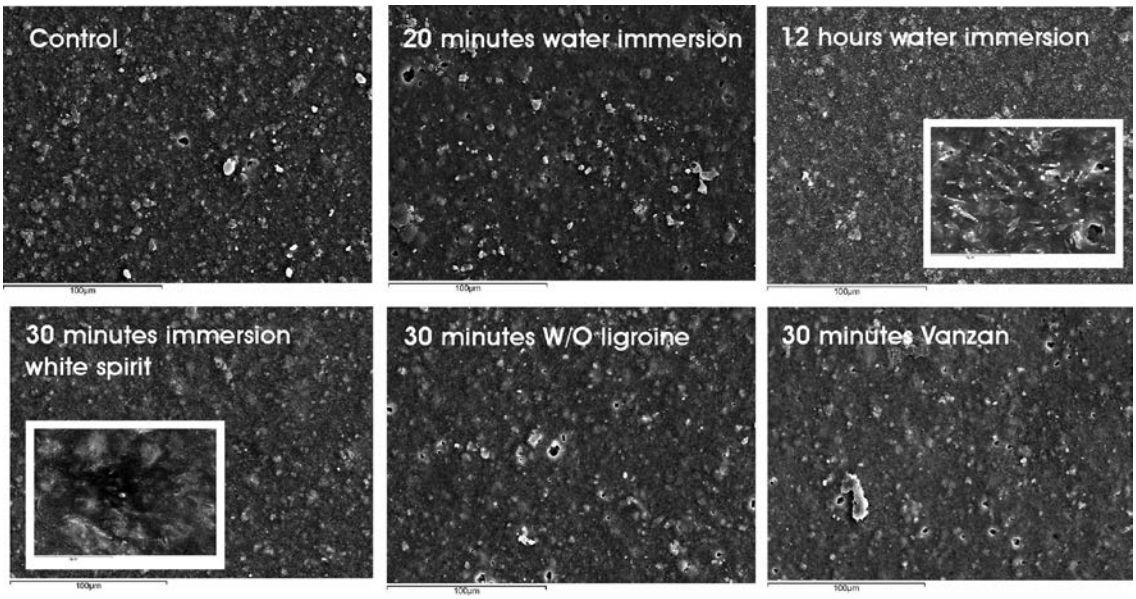


FIGURE 8. The SEM photomicrographs of Talens raw sienna paint films. Top row: (left) before treatment, (middle) after 20-minute water immersion, and (right) after 12-hour water immersion. Bottom row: (left) 30-minute white spirit, (middle) 30-minute ligroin W/O emulsion, and (right) 30-minute Vanzan gel. Details magnified at 10,000×.

Identification of Additives

The UV-Vis spectrophotometry and Fourier transform infrared spectroscopy confirmed the presence of nonionic polyethoxylate surfactants as the major component of the aqueous extracts from both PVAc and acrylic paints. Interestingly, in the PVAc aqueous extracts there were also noticeable IR absorption bands ascribed to a cellulose ether-type compound that is commonly used as a paint thickener.

Further analysis of the dried aqueous extracts of PVAc paints by means of Py-GC-MS enabled the identification of other minor additives, such as a phosphate-type compound (flame retardant), methenamine (preservative), and styrene and methacrylic acid (Silva et al., 2010). The presence of these compounds reflects the complex formulation of these paints. In this case, a small amount of an acrylic emulsion was probably added in order to improve the final properties of the paint. Additionally, in the extracts of solvents with lower polarity, such as acetone or ethyl acetate, a small amount of pigment was identified in paints where a synthetic organic pigment was used. For example, a characteristic UV absorption band associated with an organic pigment was identified in a burnt umber–based color. This suggests the addition of an organic pigment to enhance the optical properties of the paint.

ALTERNATIVE METHODS FOR CLEANING ACRYLIC FILMS: GELS AND LIGROIN W/O EMULSIONS

A similar approach to that previously described for water immersion was used for gels and ligroin in water emulsions (W/O) used as cleaning methods of acrylic films. Talens raw sienna film specimens were exposed to Vanzan and Klucel G gels for different amounts of time: 5, 10, 20, and 30 minutes. Another set of samples was exposed to a ligroin in W/O or immersed in ligroin for 30 minutes. The water absorption-drying data were obtained, and the mechanical properties were measured after drying the specimens for 1 to 2 months under laboratory conditions (23°C and 55% RH).

The weight increase and loss curves for Talens raw sienna films exposed to water immersion and swabs as well as in contact with different gels for 5 or 30 minutes is shown in Figure 9. This figure illustrates that the use of Vanzan gel reduces significantly the amount of water absorbed into the acrylic films compared to the immersion and swabbing data also presented. At 30 minutes, the gel is still able to provide water to the surface but significantly reduces the water penetration and swelling of the acrylic paint film. Similar results were obtained for Klucel G gels.

Four main points can be observed from these curves. First, the amount of water absorbed at a specific time is nearly the same whether the film is immersed in water or swabbed. Second, the amount of water absorbed from a gel is significantly reduced compared to immersion or swabbing, and this amount is not proportional to the time the gel is applied to the film. A 5 minute application results in half the amount of water absorbed compared to a 30 min application.

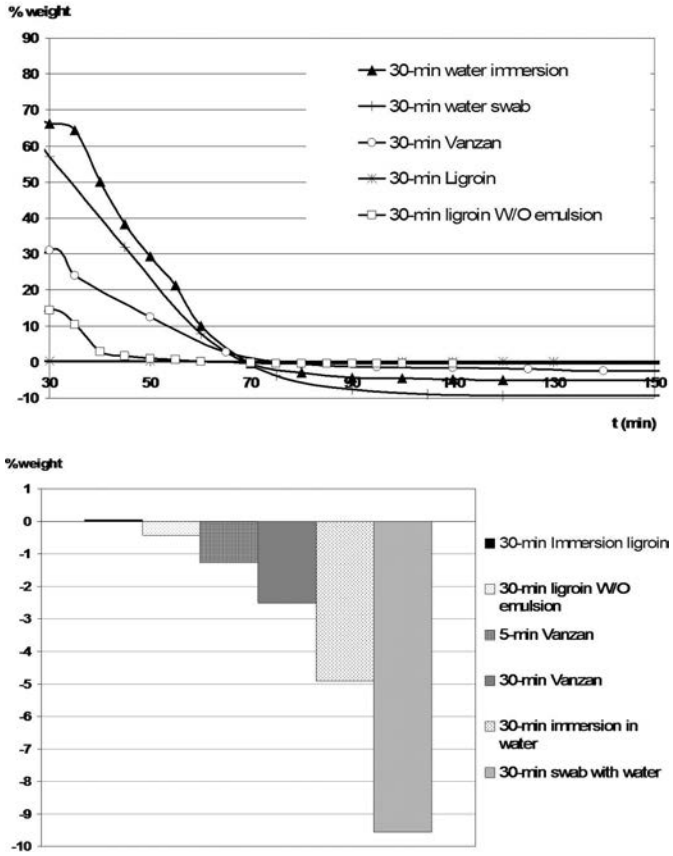


FIGURE 9. (top) Weight loss upon exposure of Talens raw sienna films to water immersion or swabbing, application of Vanzan gels, immersion in ligroin, and treatment with ligroin W/O emulsion for specified times. (bottom) Weight loss of the test paint films after application of these treatments.

Third, that 30 minute immersion in ligroin does not change the weight of the paint film significantly as this solvent is barely absorbed into the Talens acrylic films. However, it remains trapped inside the polymer chains for long periods of time, as shown by the measured weight increase. This results in a plasticizing effect of the paint film, as shown in the stress-strain curves in Figure 7. Last, that application of a ligroin W/O emulsion for 30 minutes reduces the amount of water absorbed to about half of that supplied by a gel in the same amount of time, and additive leaching was significantly reduced, as reflected by the low weight loss.

The SEM photomicrographs presented in Figure 8 clearly show that the surfaces of the test specimens were less affected when treated with gels, such as Vanzan, than when subjected to water immersion. This means that surface cleaning can be adjusted to control the risk of leaching and removal of additives using gel systems based in water.

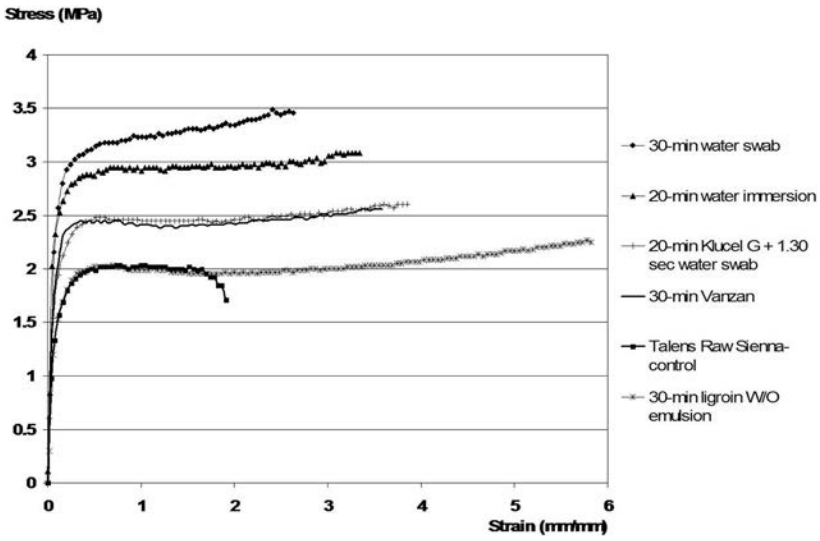


FIGURE 10. Stress-strain plots for acrylic Talens raw sienna paint films subjected to water immersion, water swabbing, Klucel G gels with and without rinsing, Vanzan gels, and ligroin W/O.

The effects of these gels on the mechanical properties of these acrylic paint specimens are illustrated in Figure 10 using the example of the Talens raw sienna. The use of the Vanzan gel on the paint film surface did not significantly affect its mechanical properties until 30 minutes of exposure to the gel had been reached. After this, the specimens started to exhibit a slight increase in stiffness, even though there was no alteration in the elongation-at-break values. Specimens treated with Klucel G gel showed a similar behavior.

It is also evident that 30 minute water swabbing affects the films more than 20 minute water immersion. The application of the ligroin W/O emulsion did not result in any significant change in the mechanical properties of the film as there was a lower extraction of paint additives.

It is important to highlight that some acrylic colors such as Liquitex Heavy Body phthalocyanine blue and naphthol red showed high sensitivity to the W/O emulsion cleaning treatments because of the presence of a surfactant in the emulsion. A simple solubility test showed that ligroin with a surfactant was able to dissolve the paint film, and that this solvent plus surfactant mixture gave the solvent the power observed with the ligroin W/O emulsion system. These points are important to bear in mind when performing the solubility tests prior to the cleaning treatment itself.

CONCLUSIONS

This study has shown that, in general, the acrylic and PVAc paints tested readily absorbed water during the immersion tests. The water absorption and swelling were evident within the first few minutes of immersion. For longer immersion times, both 20 minute and 12 hour tests, the absorbed water took roughly 2 to 4 hours to dry, and the residual water required at least 1 to 2 days for complete elimination. Some paint films, such as the PVAc Flashe burnt sienna, exhibited longer water retention times that could be attributed to the presence of clay minerals in the paint films.

For the same commercial brand, the absorption of water and the swelling effect were dependent on the pigments, fillers, and, especially, the additive content present in each color formulation. In general, synthetic colors were more prone to water absorption than inorganic ones. All films lost weight after complete drying. This could be related to the extraction of water-soluble additives, which has been shown to be a time-dependent process. Consistently, the films that exhibited more weight loss were those that absorbed more water. This was evident for Liquitex Heavy Body and also Talens colors.

The analysis of the water extracts from the immersion tests revealed the presence of different additives depending on the type of paint. In the case of the acrylics studied, a nonionic surfactant and, to a lesser extent, an anionic polyethoxylate surfactant were the major components of the extracted materials. This mixture of surfactants and an ether cellulose-type thickener were the major compounds found in PVAc Flashe paints.

Water cleaning results in the dissolution of additives, and long exposure times to water have been shown to affect the polymer lattice. This effect should be taken into account when considering the probable repeated exposures to water as a result of successive cleaning interventions over time. On the other hand, cleaning with solvents of lower polarity readily enables the dissolution of polymer chains and additives, especially if combined with mechanical action, e.g., swabbing. The solubilization of polymer chains and additives severely affected the mechanical properties of the paint films, making them far more brittle and thus more susceptible to damage and loss.

As an alternative to the more general water and solvent cleaning methods, a preliminary study on the effects of gels such as Vanzan and Klucel G as well as ligroin W/O emulsions was also carried out. The use of water gels reduced the overall effects

of water in the paints tested (absorption into the bulk film, increase in stiffness, and decrease of flexibility). The same was true for the water in oil emulsion system tested. The use of these products as cleaning alternatives to pure water appears to be a fruitful field to explore for cleaning modern materials.

It should be of interest to broaden the test sample matrix since it became clear that for different paint brands, and even for different colors within each brand, there was a variable sensitivity to the different treatments applied. In cleaning modern paints the phrase "each painting is unique" is definitely applicable, and cleaning tests should be conducted before using any of the cleaning products discussed here.

Acknowledgments

Financial support from the Spanish "I+D+I MEC" project CTQ2008-06727-C03-01 and 02/BQU supported by ERDEF funds, the "Generalitat Valenciana" I+D project ACOMP/2009/171, and the AP2006-3223 project ascribed to the Program of Predoctoral Research Fellowships for University Professors and Researchers in Spanish Universities and Research Centers from the Ministerio de Educación y Ciencia (MEC) is gratefully acknowledged. We also thank M. Planes i Insausti and J. L. Moya-López, technical supervisors responsible for the Electron Microscopy Service of the Universidad Politécnica de Valencia.

REFERENCES

Belaroui, F., M. P. Hirn, Y. Grohens, P. Marie, and Y. Holl. 2003. Distribution of Water-Soluble and Surface-Active Low-Molecular-Weight Species in Acrylic Latex Films. *Journal of Colloid and Interface Science,* 261:336–348. http://dx.doi.org/10.1016/S0021-9797(03)00098-5.

Doménech-Carbó, M. T., E. Aura-Castro, J. Mas-Barberá, and M. L. Martínez-Bazán. 2006a. Evaluation of Morphological Changes of Aged Acrylic, Ketone and Hydrocarbon Resins Used in Contemporary Artworks. *Arché,* 1:161–164.

Doménech-Carbó, M. T., G. Bitossi, D. J. Yusá-Marco, and L. Osete-Cortina. 2006b. Characterization of Changes in the Chemical Composition of Aged Acrylic Resins Used in Contemporary Artworks. *Arché,* 1:157–162.

Juhué, D., and J. Lang. 1993. Effect of Surfactant Postadded to Latex Dispersion on Film Formation: A Study by Atomic Force Microscopy. *Langmuir,* 9:792–796.

Juhué, D., Y. Wang, J. Lang, O. Leung, M. C. Goh, and M. A. Winnik. 1995. Surfactant Exudation in the Presence of a Coalescing Aid in Latex Film Studied by Atomic Force Microscopy. *Journal of Polymer Science, Part B: Polymer Physics,* 33:1123–1133. http://dx.doi.org/10.1002/polb.1995.090330716.

Kientz, E., and Y. Hall. 1993. Distribution of Surfactants in Latex Films. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 78:255–270. http://dx.doi.org/10.1016/0927-7757(93)80331-8.

Mills, J. S., and P. Smith, eds. 1990. *Cleaning, Retouching and Coatings: Preprints of the IIC Brussels Congress.* London: International Institute for Conservation.

Ormsby, B., and T. Learner. 2009. The Effects of Wet Surface Cleaning Treatments on Acrylic Emulsion Artists' Paints. *Reviews in Conservation,* 10:29–42.

Osete-Cortina, L., and M. T. Doménech-Carbó. 2006. Characterization of Acrylic Resins Used for Restoration of Artworks by Pyrolysis-Silylation-Gas Chromatography/Mass Spectrometry with Hexamethyldisilazane. *Journal of Chromatography A,* 1027:228–236. http://dx.doi.org/10.1016/j.chroma.2006.05.081.

Silva, M. F., M. T. Doménech-Carbó, L. Fuster-López, M. F. Mecklenburg, and S. Martin-Rey. 2010. Identification of Additives in Poly(vinylacetate) Artist's Paints Using Py-GC-MS. *Analytical and Bioanalytical Chemistry,* 397:357–367. http://dx.doi.org/10.1007/s00216-010-3505-2.

Wedin, P., and L. Bergström. 2005. Migration and Precipitation of Soluble Species during Drying of Colloidal Films. *Journal of Colloid and Interface Science,* 281:146–154. http://dx.doi.org/10.1016/j.jcis.2004.08.023.

Zumbühl, S., F. Attanasio, N. C. Scherrer, W. Müller, N. Fenners, W. Caseri. 2006. "Solvent Action on Dispersion Paint Systems and the Influence on the Morphology-Changes and Destruction of the Latex Microstructure." In *Modern Paints Uncovered: Proceedings from the Tate Modern Symposium*, ed. T. Learner, P. Smithen, J. Krueger, and M. Schilling, pp. 257–268. Los Angeles: The Getty Conservation Institute.

Extended Abstract—A Preliminary Study into the Effects of Cleaning Polyvinyl Acetate Paints

Ana Pereira, Maria João Melo, Peter Eaton, Stephan Schäfer, and Tom Learner

INTRODUCTION

The effects of cleaning treatments on paintings made with synthetic paints are a major concern for conservators of modern and contemporary art. Synthetic paints typically include a complex mixture of additives that are likely to influence the paint's response to different treatment methods, and their high sensitivity to most organic solvents narrows the choice of products that can be used. Knowledge gathered during cleaning of traditional oil or egg tempera paintings can clearly not be directly correlated to contemporary paintings. It is widely recognized by the conservation profession that further research into the chemistry and properties of synthetic paints and their response to conservation practice is therefore urgently needed.

This study presents the preliminary results on the effects that selected cleaning methods have on test films of polyvinyl acetate (PVAc) paint and discusses implications for cleaning paintings by Julião Sarmento (born 1948). He is one of the most prominent contemporary Portuguese artists who made wide use of PVAc paints (Pereira et al., 2007). In the 1990s he started a series of paintings, commonly called the White Paintings, that require surface cleaning already because of a combination of their monochromatic white backgrounds and affinity for dirt pickup.

MATERIALS AND METHODS

Samples of a PVAc emulsion paint containing titanium dioxide (rutile form) were artificially aged using a xenon arc light source for 3250 hours. During this irradiation, the mock-ups were exposed to dirt particles, i.e., atmospheric particulates. Commonly used cleaning methods were subsequently tested: water, water and a nonionic surfactant (Brij700S), and white spirit. Use of a soft eraser (Akapad White) was also examined to reproduce a real case of cleaning a work by Sarmento. White spirit was included since aliphatic mineral spirits are known to have a minimal effect on acrylic paints (Ormsby and Learner, 2009), another main class of synthetic emulsion paints. Two samples were used for each test, except for the white spirit.

***Ana Pereira** and **Maria João Melo**, Departamento de Conservação e Restauro and Requimte Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Caparica, Portugal. **Peter Eaton**, Requimte, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal. **Stephan Schäfer**, Departamento de Conservação e Restauro, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Caparica, Portugal. **Tom Learner**, Contemporary Art Research, Getty Conservation Institute, 1200 Getty Center Drive, Los Angeles, California 90049-1684, USA. Correspondence: Ana Pereira, ana.pereira@campus.fct.unl.pt; Maria João Melo, mjm@fct.unl.pt; Peter Eaton, peter.eaton@fc.up.pt; Stephan Schäfer, schaef@fct.unl.pt; Tom Learner, tlearner@getty.edu.* *Manuscript received 19 November 2010; accepted 24 August 2012.* *Contributions to this paper by T. Learner are Copyright © 2013 The J. Paul Getty Trust, all rights reserved.*

In order to ensure reproducibility and accuracy in the cleaning operation, mock-ups were immersed in the cleaning solution and tests were run in duplicate. As previous reports show that most of the material lixiviated from a paint sample occurs in the first few minutes (Ormsby and Learner, 2009), the effect of a five-minute immersion was evaluated.

The effects of cleaning (both efficacy of dirt removal and changes to the paint film) were assessed by the following: level of dirt removal, color change, loss of extractable material, detection of residues, and disruption to the paint surface. Changes to the paint surface morphology were monitored by atomic force microscopy (AFM) in vibrating mode on areas of 50×50, 10×10 and 2×2 μm^2. Alterations in the surfaces' chemical composition were assessed by Fourier transform infrared spectroscopy attenuated total reflectance (ATR), and color coordinates were collected with a portable colorimeter, using the CIE L*a*b* system. Roughness values R_a obtained with AFM were calculated on the 10×10 μm^2 scan areas, as an average of five selected 2×2 μm^2 areas. The value presented is the average of the two replicates.

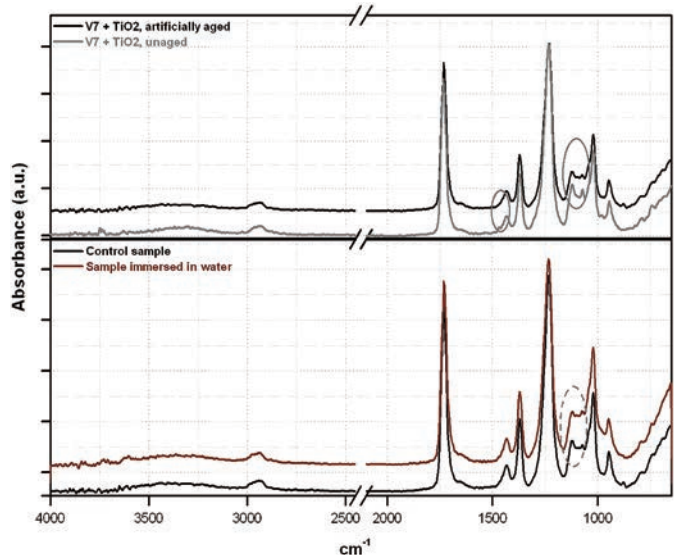


FIGURE 1. The ATR infrared spectra. (top) Artificial aging of the sample induces loss of the plasticizer, as seen from comparison of the circled peaks. (bottom) The aged control sample shows no plasticizer enrichment on the surface, and therefore only minor differences can be observed in those peaks after water immersion.

RESULTS AND DISCUSSION

Artificial aging studies indicate that loss of paint plasticizer, diisobutyl phthalate (DiBP), is the major alteration between aged and unaged samples (Ferreira et al., 2010). The ATR spectra from the artificially aged control sample showed no significant signs of a surface enrichment with DiBP. Therefore, it was expected that immersion could only remove negligible quantities of plasticizer still present on the tests films. As expected, only minor changes were seen in ATR spectra that can be tentatively correlated to the extraction of this additive (Figure 1). Moreover, DiBP was not detected among the residues remaining after immersion.

Because of the irregular surface topography and affinity for dirt that is retained by the paint surface, immersion of the samples was not efficient for dirt removal. This was confirmed both by optical microscopy and colorimetry.

Smaller AFM scan areas were found to be the most useful because of the heterogeneous nature of the paint surface and the technical difficulties encountered when scanning large features deposited on the samples. Moreover, with the 10×10 and 2×2 μm^2 areas changes in the latex surface can be seen with high detail (Figure 2). Pure water did not induce relevant alterations on the morphology of the white paint. However, with the aqueous solution of Brij700S the smoothness of the latex particles is lost, and the polymer surface displays a more irregular texture, which could be the result of surfactant residues left on the paint. Large and protruding features appeared on the paint's surface after white spirit immersion.

Cleaning with an eraser resulted in both particles and/or eraser additives being left on the surface. These residues could not be identified with ATR, probably because of their small quantity, but they are clearly related to the eraser because the pattern left in the polymer surface is similar to that observed when using it directly on mica sheets. Moreover, the physical abrasion provoked by the mechanical action can account for the decrease in the surface roughness.

CONCLUSIONS

These preliminary results offer a first insight into the response of PVAc emulsion paints to cleaning procedures. Surface roughness was not significantly affected with the immersion of the samples in any of the tested solvents. However, changes in surface morphology were observed for the surfactant solution and even more for the white spirit. Immersion of the samples was insufficient to obtain dirt removal. Moreover, surfactant residues were not effectively removed. The most significant changes were introduced by the eraser. Concern should be raised about using Akapad for dirt removal in Sarmento's White Paintings as these paints might be liable to mechanical damage. Physical disruption of the latex paint was only detected at the nanoscale; however, it could result in a flattening of the paint surface that is contrary to the distinctive pigment agglomerates and filler texture typical of these paintings. Work is currently under way to study and test samples prepared by the artist and naturally aged (20 years) as well as on model samples reproducing the artist's technique.

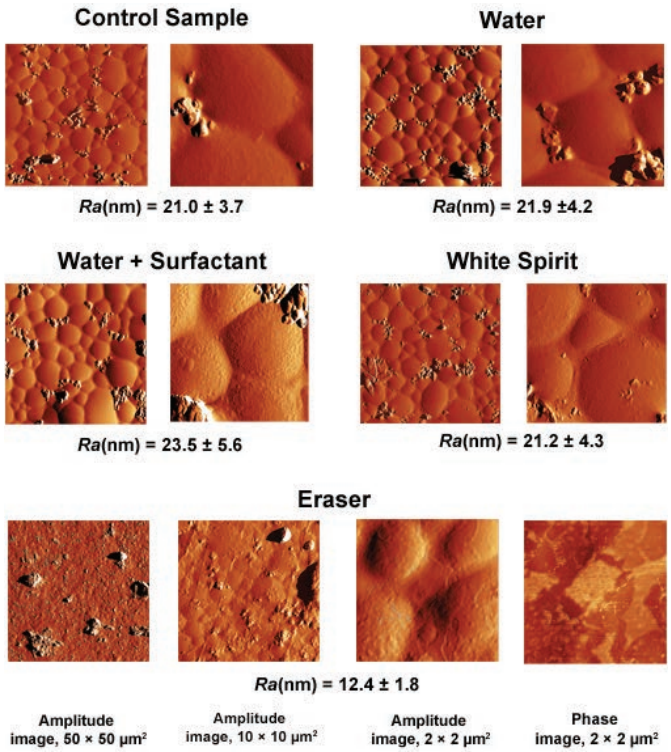


FIGURE 2. The AFM amplitude images of artificially aged PVAc white paints. For the aged control and solvent-immersed samples, images of surface areas are presented ($10 \times 10\ \mu m^2$ at the left and $2 \times 2\ \mu m^2$ at the right); area sizes for the erased samples are indicated below the images. Average roughness R_a is listed below each sample.

Acknowledgments

Ana Pereira acknowledges Fundação para a Ciência e Tecnologia (FCT/MCTES) for her Ph.D. grant (SFRH/BD/39917/2007) and Joana Lia for kindly providing the paint samples. This work has also been supported by Fundação para a Ciência e a Tecnologia through grant no. PEst-C/EQB/LA0006/2011.

REFERENCES

Ferreira, J. L., M. J. Melo, and A. M. Ramos. 2010. Poly(vinyl acetate) Paints in Works of Art: A Photochemical Approach. Part 1. *Polymer Degradation and Stability,* 95:453–461. http://dx.doi.org/10.1016/j.polymdegradstab.2010.01.015.

Ormsby, B., and T. Learner. 2009. The Effects of Wet Surface Cleaning Treatments on Acrylic Emulsion Artist's Paints—A Review of Recent Scientific Research. *Reviews in Conservation,* 10:29–41.

Pereira, A. I., S. Schäfer, and M. J. Melo. 2007. "Julião Sarmento, a Portuguese Artist at Work: Study of *Just a Skin Affair* from 1988." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. J. S. Learner, P. Smythen, J. W. Krueger, and M. R. Schilling, pp. 294–295. Los Angeles: The Getty Conservation Institute.

The Modular Cleaning Program in Practice: Application to Acrylic Paintings

Chris Stavroudis and Tiarna Doherty

ABSTRACT. The Modular Cleaning Program (MCP) is both a computer database system and an approach to cleaning using premixed concentrates that allows the rapid prototyping of cleaning solutions. The MCP is designed to assist the conservator in refining the cleaning of artworks by allowing more cleaning options to be tested in a fast and convenient way. Because the software component works from a database of physical and chemical properties and first principles, the MCP is well positioned to incorporate this newfound understanding of acrylic paint systems into its cleaning schema. As we gain insight into the cleaning of acrylic paint, we can tailor the range of variations offered by the MCP. The special considerations that are brought to the cleaning of acrylic emulsion paints are consequences of the complexity of the paints themselves. There are numerous components in an acrylic paint film. By examining the sensitivity and susceptibility of the various additives, we can anticipate which cleaning conditions may lead to swelling or damage to the paint film and which cleaning strategies will lead to more successful outcomes. By controlling the pH and the ionic strength (as indicated by conductivity), the conservator can minimize the aqueous cleaning systems' effect on the paint film.

INTRODUCTION

Recent progress in the cleaning of paint surfaces has been supported by a number of factors. Since the mid-1980s, Richard Wolbers at the Winterthur/University of Delaware Program in Art Conservation has been developing cleaning systems to assist conservators (Wolbers, 2000). These systems and his thought processes have been communicated to the conservation community through his workshops and lectures, his book and other publications, and a flow of students who have studied under him. His work brought, and continues to bring, a fresh focus on the intersection of conservation science with conservation practice.

Advances in chemistry and analytical instrumentation have allowed more subtle and nuanced conservation questions to be researched. We now possess tools that can be used to investigate details of the cleaning processes in ways that were inconceivable a generation ago. Also, advances in biochemistry, material science, and a number of the newly evolved hyphenated disciplines have supplemented our knowledge.

Industrial advances driven by increased sophistication in chemical engineering and manufacturing have created technologies and materials that have been repurposed and adapted in conservation. Concern for the environment also drives conservators to look for new approaches to old problems and to minimize the impact on their health and safety and the global environment.

***Chris Stavroudis**, 1272 North Flores Street, West Hollywood, California 90069-2904, USA. **Tiarna Doherty**, Painting Conservation, J. Paul Getty Museum, 1200 Getty Center Drive, Suite 1000, Los Angeles, California 90049, USA. Correspondence: Chris Stavroudis, cstavrou@ix.netcom.com; Tiarna Doherty, tdoherty@getty.edu.* *Manuscript received 19 November 2010; accepted 24 August 2012.* *Contributions to this paper by T. Doherty are Copyright © 2013 The J. Paul Getty Trust, all rights reserved.*

Cleaning traditional paint surfaces has a long history of practice, research, the occasional failure, and exciting new developments. In contrast, the cleaning of acrylic paint surfaces has been recognized only recently as a process distinct from the cleaning of historical and other modern paint systems (Jablonski et al., 2010). We are now beginning to look critically at acrylic paints, to investigate and attempt to understand their characteristic behavior, and to base cleaning systems on that understanding.

As research advances in the formulation, aging, and degradation of acrylic paints, cleaning systems used by conservators are evolving to incorporate these developments and related insights. As an adaptable tool designed to facilitate methods of cleaning, the Modular Cleaning Program is capable of integrating advances in our knowledge of acrylic paints and the practices for cleaning them.

DIFFERENT PARADIGMS IN THE CLEANING OF PAINTED SURFACES

Wolbers' work, along with work by numerous other conservators and conservation scientists, has led to a number of new approaches to cleaning. More significantly, these new approaches have encouraged a more nuanced consideration and understanding of cleaning.

Wolbers' concept of "recovering a surface" or "unpacking" layers of unoriginal materials on a painting's surface is driven by the desire to control the aesthetics of the cleaning. These phrases have evolved to describe a process in which the collection of materials that are to be cleaned from a painting's surface are considered both individually and as layers or a mixture, and they are selectively removed. They reflect a change in approach and an interest in subtlety that has entered conservation lexicon not because they are new concepts, but because new cleaning techniques have given conservators the ability to strive for this precision.

THE MODULAR CLEANING PROGRAM

The Modular Cleaning Program (MCP) is a direct outgrowth of the Gels Research Project, a collaboration between the Getty Conservation Institute; California State University, Northridge; the Winterthur/University of Delaware Program in Art Conservation; and the Conservation Division of the Winterthur Museum. The goal of the Gels Research Project was to systematically investigate the problem of residues left on surfaces after cleaning with a system that contained nonvolatile components. One portion of the project, represented by the publication by Stulik and Wolbers (2004), was an attempt to codify Wolbers' thinking process, his "logic tree," for choosing a cleaning system. In its initial phase, the MCP was an amplification of the material presented in that publication. Originally designed to manage aqueous cleanings, the system was expanded to work with free solvents, Carbopol-based solvent gels, and, most recently, Pemulen-based emulsions. The MCP is an evolving tool to help the conservator achieve precision in designing a cleaning system. It does not direct the conservator on how to clean a surface, but rather organizes cleaning options in a logical and expandable way.

The MCP refers to two distinct aspects of the system. "Program" refers to a computer program built from databases of physical properties combined with software routines that model the interactions of components in a cleaning system. "Modular" refers to a set of concentrated stock solutions, with formulae generated by the database from the conservator's specifications, that can be mixed in various ways, allowing multiple cleaning systems to be formulated and tested quickly and easily.

Using the appropriate theory, the MCP models the chemistry of each broad class of physical and chemical interaction. The MCP has 19 internal databases, but the conservator interacts directly with only a few, one being the components database, an extensive repository of physical constants for each chemical entity used to build a cleaning system. A useful resource in and of itself, the components database includes various chemical names; Chemical Abstracts Service registry number; molecular weight; physical form; density; acid dissociation constants for weak acids and bases; formation constants for chelating agents; hydrophile-lipophile balance (HLB) number, critical micelle concentration (cmc), aggregation number, and cloud point for surfactants; and boiling point, Hildebrand, Hansen, and Teas solubility parameters, dipole moment, index of refraction, dielectric constant, and molar volume for solvents. There is also a separate database of binary and ternary azeotropes for solvent mixtures. The MCP accesses the relevant physical constants as it calculates cleaning formulations in the solutions database, another of the databases actively used by the conservator.

The solutions database models mixtures of chemicals from the components database from simple aqueous solutions to mixtures of acids and bases, mixtures of solvents, and Carbopol-based solvent gels. The entries in the solutions database are the stock solutions that are used to mix prototype cleaning systems.

Aqueous solution calculations are based on the appropriate physical constants from the components database and user-specified data. For pH buffer and chelating agent solutions, acid dissociation constants and user specifications of counterions, cleaning solution concentrations, and pH values are used to calculate the concentrations of ionic and molecular species in solution and the amount of the counterion necessary to set the solution to the specified pH. Solvent mixtures are modeled in Hansen three-dimensional space, although Teas and Hildebrand parameters are calculated as well. The solvent phase of Carbopol-based solvent gels and Pemulen-based emulsions are modeled as simple solvent mixtures. The gel phase of solvent gels is based on stoichiometric relationships between the Carbopol, the user-specified organic amine or amines used to neutralize the Carbopol, and the inferred stoichiometric amount of water necessary to form a gel. The aqueous phase of Pemulen-based emulsions is modeled as an aqueous cleaning solution thickened with Pemulen to which a solvent or solvent mixture is added.

Aqueous cleaning systems are modeled as a set of five orthogonal components in the MCP. That is to say, pH, ionic strength, the presence or absence of a chelating agent, the presence or absence of a surfactant, and the presence or absence of a gelling agent can each be manipulated as independent variables. (This is not strictly the case. For example, when a chelating agent is added to a solution, the ionic strength will increase dramatically. However, the computational model used in the MCP is flexible enough to account for these interdependencies.)

When building a pH buffer solution in the solutions database, the conservator chooses the working pH (through the selection of the buffer), the neutralizing base or acid, and the buffer's concentration in the final cleaning solution. Likewise, when building a chelating solution, the conservator specifies which chelating agent to use, the neutralizing base, the solution pH, and the working concentration. For surfactant solutions, the surfactant concentration can be specified by the conservator in terms of the cmc or, if the aggregation number is known, in micelle moles. In addition, recent modifications to the MCP allow the conservator to add an organic cosolvent to the aqueous cleaning solution.

One of the strengths of using a system that models the various solution interactions as the basis of the computational model is that the user can specify the demands of different types of cleanings. This flexibility built into the MCP allows the conservator to modify cleaning solutions and strategies on the basis of advances in conservation science as well as research from other industries. Thus, advances being made in the study of acrylic paints can be incorporated into a cleaning schema specific for these paint surfaces.

CONSIDERATIONS AND COMPLICATIONS IN THE CLEANING OF ACRYLIC PAINT SURFACES

The decision to clean an acrylic surface is never taken lightly by conservators, curators, or conservation scientists. Although acrylic paints are in many ways remarkably durable, the surfaces are rather fragile. This fragility, coupled with the tendency for the paintings to be quite large, leaves them vulnerable to damages from handling. Fingermarks and scuffs can be disfiguring and difficult to ameliorate. The gradual accumulation of surface grime is a more general concern. Druzik and Cass (2000) have shown that even in a presumably benign museum environment the slow accumulation of surface grime will lead to a discernible visual alteration of a paint surface after approximately 50 years. This means that the cleaning cycle for acrylic paint surfaces has begun.

Research by a number of conservators and conservation scientists has begun to identify some of the special properties of acrylic paints (Hayes et al., 2007; Ormsby et al., 2007; Ormsby and Smithen, 2008). That research, along with experience from treatments, both successful and less than successful, has advanced our understanding of the special challenges posed by the cleaning of acrylic paint surfaces.

Examination of acrylic paint formulations (such as Croll, 2007; Wolbers et al., this volume) provides clues about the variables that must be considered when devising a cleaning strategy for these paint surfaces. The base of an acrylic emulsion paint system is the acrylic emulsion itself. It is created from water, the acrylic monomer (or monomers), and materials to stabilize the monomer(s) into micelles, control the pH, initiate the polymerization reaction, and prevent foaming. Additional ingredients, thickeners and coalescing agents, among others, transform it into a successful paint binder (termed the letdown). Separately, pigments and extenders must be mixed with water, dispersing agents, and other components (termed the grind as this is what is actually dispersed in a roller mill as the acrylic binder cannot be milled) that are then added to the letdown forming the acrylic emulsion paint. All of these materials make for a far more complicated and interdependent system than any traditional paint system.

One can attempt to predict the potential sensitivity of the paint on the basis of the sensitivities and properties of each of these many components. These potential sensitivities can be categorized into broad classes of concern: the effects of pH, the effects of ionic strength, and the effects of surfactant migration.

Before discussing these concerns, it is important to consider the physical structure of the acrylic paint film. Acrylic emulsion paints dry differently from other paint systems (Figure 1). The initial drying is by evaporation of much of the water, leaving the pigments and spherical polymer containing micelles to form a close-packed matrix. (In the absence of other ingredients, the acrylic emulsion will form into a hexagonal close-packed arrangement.) The next stage in drying is for the water held by capillary forces between the polymer spheres and pigment particles to evaporate, pulling the spheres into intimate contact. Coalescing agents and the nature of the polymer itself allow the spheres to diffuse into adjacent spheres, forming a film (Zumbühl et al., 2007). Ideally, the resulting film would be continuous, but it is not.

A number of factors will affect the degree to which the coalescing of the polymer spheres occurs. The resulting structure of the film will fall somewhere between the solid membrane of a fully coalesced film and an inhomogeneous structure with pores, irregularities, and imperfections. This physical structure of the acrylic film has particular implications when considering surfactant migration and the ionic strength of cleaning systems.

THE PH OF CLEANING SOLUTIONS

Poly(acrylic acid) (PAA) thickeners, such as Primal ASE-60, a sodium salt of PAA, are added to acrylics to modify the consistency of the paint. Acrylic paints fresh out of the tube are formulated to have a pH around 9.5 (Learner, 2004:12), assuring that the PAA acid groups are deprotonated and fully elongated, forming a three-dimensional structure that gives the acrylic paint the creamy texture expected by artists. When the paint dries, the PAA hardens but retains the potential to respond to the pH of an aqueous cleaning system. In an alkaline (or even neutral) cleaning

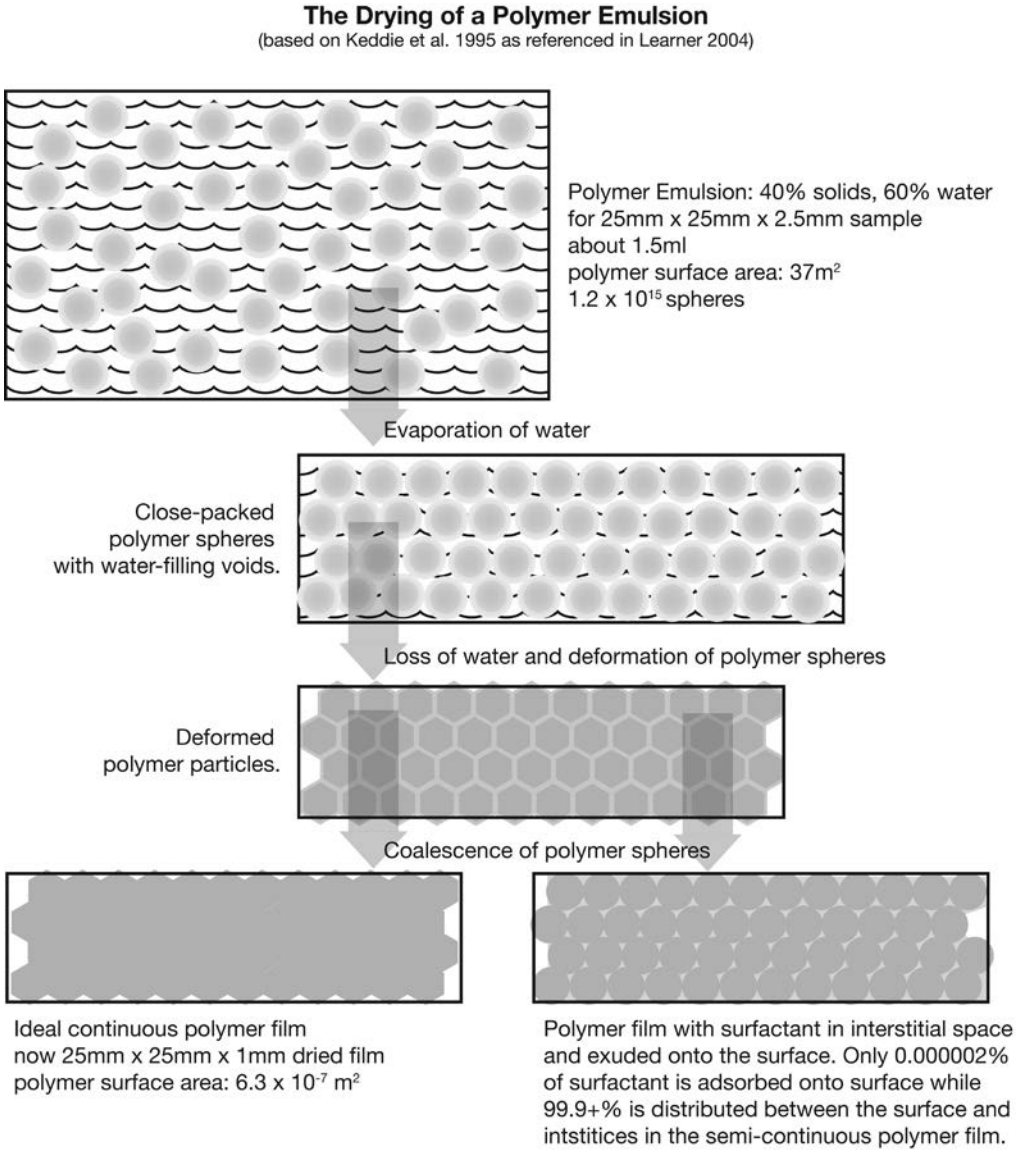


FIGURE 1. The drying of a polymer emulsion occurs in three stages: (1) evaporation of water from the bulk solution, (2) evaporation of water held by capillary forces, and (3) coalescence of the polymer spheres into the final film.

environment, the polymer will hydrate and swell, softening and disrupting the surface of the paint film. (This is a familiar process witnessed by conservators when working with Carbopol resins, also a PAA.) However, at a sufficiently low pH, the acid groups on the PAA molecules will remain in their less-soluble acid form and will be minimally affected by an aqueous cleaning system.

Recent research confirms this sensitivity. The results of high-throughput (HTP) testing conducted at the Dow Chemical Company in a collaborative project between the Getty Conservation Institute, the Tate, and Dow (Phenix et al., In press) have demonstrated that lower-pH cleaning systems are safer for acrylic paint surfaces. The HTP testing compared the degree of cleaning of artificially soiled and aged acrylic paint surfaces with different pH cleaning solutions. The greatest removal of the soiling was found to occur at a pH of 4 and 5. At a pH of 6, cleaning was less effective. At a pH of 7 and 8, the surfaces were found to have lightened closer to their original color; however, the cleaning was found to have removed a swollen layer of paint from the test surface and not simply removed the grime without affecting the paint.

To minimize the swelling of PAA thickeners, the pH of the cleaning system has to be kept as low as possible. Additionally,

maintaining the chosen pH of any cleaning solution while it interacts with a paint surface is of critical importance. With the MCP, this control is achieved by the inclusion of a buffer system in every aqueous cleaning system.

The choice of buffer is based on the acid dissociation constant (the pK_a) of the weak acid or base and the target pH of the buffer solution. The MCP provides the conservator with information on the effective buffer range of a given weak acid or base. After the conservator chooses the neutralizing base or acid to set the pH of the buffer solution, the MCP makes a first approximation calculation of the amount of neutralizing component to add to obtain the desired pH. Because the calculation is only a first approximation, the final pH of all of the stock solutions in the MCP need to be checked and adjusted as they are being made using a calibrated pH meter.

IONIC STRENGTH

As mentioned above, the dried acrylic paint film is not completely coalesced. It is an imperfect film that will have physical properties somewhere between those of an impermeable film, a semipermeable membrane, and a spongelike, microporous surface.

If an aqueous cleaning system is applied to paint that behaves like an impermeable membrane, we can reasonably expect nothing to happen to the paint film as the surface is cleaned. If a cleaning solution is applied to a semipermeable membrane, interactions between the paint and liquid will be driven by osmotic forces. If it is applied to a paint that behaves like a microporous surface, the interaction between the solution and components in the paint will be driven by simple diffusion.

When an aqueous solution is placed on the surface of a microporous paint film, the relative concentration of soluble salts in the paint will want to be in equilibrium with the ionic solutes in the cleaning solution. If distilled water is placed on the surface of the paint film, the higher ionic strength inside the paint film will cause the diffusion of the ionic species into the water, leaching original material out of the paint film. When the cleaning solution is of lower ionic strength than the paint, the cleaning solution is referred to as hypotonic.

If the cleaning solution has more ionic species than the paint film, ions from the cleaning solution will diffuse into the paint film. The cleaning solution in this case would be hypertonic to the paint film.

If, however, the ionic strengths of both the cleaning solution and the paint film are more or less the same, although there may be some ionic exchange between the solutions, there will be no net movement of ions into or out of the paint layer. In the porous paint film model, a cleaning solution that is isotonic to the paint is clearly desirable.

Considering the acrylic paint film as a semipermeable membrane rather than a microporous film, we can expect to see osmotic effects when a cleaning solution is applied to the paint film. If distilled water is placed on the acrylic paint surface and the film acts like a semipermeable membrane, the water will be drawn into the paint film, causing rapid swelling of the paint. This hypotonic scenario is clearly not desirable.

If a cleaning solution with a high ionic strength is placed on the acrylic paint surface and that surface behaves only as a semipermeable membrane, static pressure could develop inside the paint film. However, as the dried acrylic paint film does not contain free water, the hypertonic solution presumably cannot drive transport through the film. If an isotonic solution is applied to the semipermeable surface of an acrylic paint film, osmotic pressure will neither drive water into the paint film nor attempt to draw water out.

Whether the paint in fact behaves as a microporous film or a semipermeable membrane, it is clear that a cleaning solution that is isotonic to the paint film is the safest way to approach an aqueous cleaning. Therefore, it is important that the ionic environment inside an acrylic paint film be understood and that cleaning as well as rinsing or clearing solutions be isotonic to the paint film.

It should be noted that osmotic pressure can also be caused by nonionic water-soluble species as well. Further research may show that both ionic and osmotic buffers will be required in cleaning solutions to control osmotic effects, ionic exchange, and cleaning efficiency.

An obvious difficulty, of course, is determining the ionic concentration of the paint film so that a cleaning solution can be formulated to be isotonic to it. Measuring the conductivity and pH of a drop of distilled water placed on the surface for a short period of time, but long enough to allow some sort of equilibrium with the acrylic paint to be reached, gives an imperfect indication of the ionic environment of the paint film. The drop of water is placed first into a single-drop conductivity meter and then into a single-drop pH meter, both of which are commercially available. However, it is to be remembered that a drop of water on an acrylic paint surface can leave an irreversible color or texture change. While this is an imperfect means of gauging the ionic environment of the paint surface it is the only practical option available to the practicing conservator.

By using the complex aqueous cleaning option in the program, the MCP allows the conservator to control the ionic strength of the test cleaning solutions along with all of the other solution parameters managed in a simple cleaning. (The MCP calculates the test solution conductivity on the basis of measurements of the stock solutions taken at various dilutions.) Ionic strength can be lowered by decreasing the amount of buffer and chelating agents added to the test cleaning solution. If a higher ionic strength is required, an ionic buffer (typically dilute NaCl, although other salts are being investigated) can be added to the test cleaning solution.

The original design of the MCP was for cleaning traditional paint surfaces. Research by Wolbers (2000:60–61) had shown that chelating agents were most effective at approximately 20–50 mM concentration range (measured at pH 4.8). On the basis of this finding, the normal working concentrations of

chelating agents in the MCP is 50 mM. Recent results of testing cleaning efficiency through HTP testing (Phenix et al., In press) show that for acrylic paints the optimum cleaning efficiency is achieved at a concentration of 0.7% triammonium citrate, or 29 mM. With this new information, the conservator can specify that chelating agents should be used at a 29 mM concentration when used on acrylic paints.

A QUICK TRICK

One attractive and effective way to maintain a low pH and a reasonable ionic strength is to use carbonated distilled water for surface cleaning. The dissolved carbonic acid, pK_a 6.35, gives the system a low pH, and the dissolved carbonate, bicarbonate, and hydrogen ions give the solution a moderate ionic strength. Carbonated distilled water can be produced in a soda siphon, which dissolves 8 g of CO_2 into 1 L of water. The carbonated water is stored under pressure in the siphon until it is dispensed for use. Adding 1% ethanol to the distilled water before adding CO_2 produces a low-pH, moderate ionic strength solution with the ability to reduce the effective HLB of surfactants washed off of the paint's surface (described below).

THE SURFACTANT PROBLEM

As discussed above and illustrated in Figure 1, the surfactants present in the acrylic emulsion are concentrated into two areas in the dried paint film. Surfactants, which stud the surface of the dispersed emulsion, are pushed to any interfacial surface as the polymer spheres coalesce. Depending on the efficiency of the coalescing phase of drying, the surfactant must go either to the film surface or accumulate in interstitial spaces left between the coalescing polymer spheres. In pure acrylic medium this excess surfactant can be seen as cloudiness that develops on the surface of the film as the surfactant crystalizes (Hayes et al., 2007). In the actual paint it is reasonable to assume that the surfactant accumulates in discontinuities created by pigment particles and extenders as well as between incompletely coalesced polymer spheres. Considered from just the physical relationship between an acrylic emulsion and the dried paint film, the change in surface area between millions of 100 µm surfactant-studded polymer spheres to a solid slab of paint is revealing. A quick calculation comparing the surface area of the polymer spheres (1.5 mL of acrylic emulsion has a polymer surface area of approximately 37 m^2) to the dried emulsion film (approximately $25 \times 25 \times 1$ mm, a surface area of 6.3×10^{-7} m^2) shows that more than 99% of the surfactant used in the original acrylic polymerization reaction will have no surface on which to adsorb. (This assumes that the surfactant monolayer found on the emulsion particles is comparable to the adsorbed surfactant on the dried film.)

Of the surfactant that has accumulated in voids in the acrylic matrix in the final film, some will be squeezed out of the paint film to a surface by drying forces and compaction during coalescence. Research has shown that this surfactant can affect the paint in a number of ways.

Surfactant accumulating on the surface of an acrylic film can alter the gloss or saturation of the paint film (Ormsby et al., 2007). This accumulation may be a gradual process. This alteration, although inherent to the acrylic paint, can in no way be considered part of the artist's intent. However, the surfactant is original to the material of the artwork.

Surfactant has been shown to decrease the glass transition temperature T_g of an acrylic film (Smith, 2007). It is reasonable to expect that the exuded surfactant, by lowering the glass transition temperature, will function as a plasticizer of the acrylic surface. The lower T_g can facilitate the irreversible migration of grime into the acrylic film, which makes a case for the removal of the surfactant layer.

On the other hand, Ormsby and Smithen (2008) have shown that surfactant continues to be exuded from the interstitial reservoirs to the surfaces of the paint film. Further, this migration can be exacerbated by aqueous cleaning systems (Ormsby et al, 2009). It is generally presumed that the evaporation front of water, which has penetrated into the body of the acrylic paint film, carries the surfactant to the surface. This makes a contradictory case for not removing the surfactant from the surface of the paint and, in particular, not removing it in an aqueous treatment.

Although many conservators feel that removal of the surfactant layer is acceptable, the decision to remove the surfactant layer is something that must be evaluated by the conservator for each cleaning on the basis of the painting and the conditions necessitating the cleaning treatment. It is worth noting that acrylic paint manufacturer Golden Paints recommends that artists remove or reduce the excess surfactant from the surface of their paintings by rinsing with deionized water two to four weeks after the painting is finished (Hayes et al., 2007:64).

Research into cleaning has demonstrated that an aqueous cleaning will, not surprisingly, remove the surfactant layer from the surface of the paint film, whereas a low-polarity aliphatic solvent will not disrupt the surfactant layer (Ormsby et al., 2007). Unfortunately, a low-polarity solvent will rarely do anything to remove surface grime, finger marks, or accretions.

If the conservator decides to remove the surfactant layer, there is an inherent problem described by Wolbers (University of Delaware, personal communication). Consider that the surfactant from the acrylic emulsion was sufficiently powerful to form a stable emulsion of acrylic monomers in water. As this and other surfactants are pulled into solution during the cleaning, they will have an intrinsic detergency, and we can assume that this detergency will have the capacity to wash away pigment particles as well as degraded medium.

The research of the Tate-AXA project surveyed cleaning systems used by conservators (Ormsby and Smithen, 2008). One of the systems that was found to work particularly well was a solution of 1% ethanol in water. In addition to being a solvent,

ethanol is a very low HLB surfactant. (This property is exploited when it is used to lower the surface tension of water.)

Wolbers's observation is that the presence of the alcohol in the cleaning solution lowers the effective detergency of the cleaning solution. When two surfactants are mixed together, the effective HLB is the weighted average of the individual HLBs. The presence of the low-HLB ethanol in the cleaning solution will reduce the effective HLB of surfactant that is washed up from the surface of the acrylic paint and thus reduce the ability of the surfactant to assist in the suspension of pigment particles and degraded binding medium. (A 1% solution of ethanol in water with Triton X-405 added at the critical micelle concentration [HLB = 17.6, cmc = 0.16%] will have an effective HLB of 9.2, which can be expected to be far less detersive than the Triton X-405 on its own.)

By modifying the MCP to allow the incorporation of co-solvents into the aqueous cleaning system, small percentages of water-soluble organic solvents can be added to the conventional cleaning systems as formulated by the MCP. The addition of an alcohol or another surfactant will be reflected in the HLB value of the cleaning solution. This modification as well as aqueous solution sets designed specifically for use with acrylics will be available in version 4 of the MCP, which is still under development.

CONCLUSION

Although acrylic paintings can be cleaned without the use of the Modular Cleaning Program, the MCP can serve as a tool for comparing the most current theories on the cleaning of acrylic paint surfaces with the real-world results of cleanings by conservators. Functioning as a lingua franca between research and practice, the MCP can provide precise formulae and solution specifics to standardize the chemical conversation on the cleaning of acrylic surfaces.

Information on the background and use of the Modular Cleaning Program can be found in the references (Stavroudis et al., 2005; Stavroudis and Doherty; Stavroudis, 2007). The MCP software can be obtained from Conservation OnLine (CoOL; http://cool.conservation-us.org/byauth/stavroudis/mcp/). The program is freely available to professional conservators, runs under Windows or Macintosh operating systems, and does not require ownership of FileMaker Pro.

Acknowledgments

The authors give special thanks to Carolyn Tallent and Irene Konefal for their feedback over the years and in the preparation of the presentation and article.

REFERENCES

Croll, S. 2007. "Overview of Developments in the Paint Industry Since 1930." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. Krueger, and M. Schilling, pp. 17–29. Los Angeles: The Getty Conservation Institute.

Druzik, J., and G. Cass. 2000. "A New Look at Soiling of Contemporary Paintings by Soot in Art Museums." Paper presented at the Third Indoor Air Quality Meeting, Oxford Brookes University, Oxford, UK, 10–12 July. http://iaq.dk/iap/iaq2000/2000_10.htm (accessed May 2010).

Hayes, J., M. Golden, and G. Smith. 2007. "From Formulation to Finished Product: Causes and Potential Cures for Conservation Concerns in Acrylic Emulsion Paints." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. Krueger, and M. Schilling, pp. 58–65. Los Angeles: The Getty Conservation Institute.

Jablonski , E., T. Learner, J. Hayes, and M. Golden. 2010. "The Conservation of Acrylic Emulsion Paintings: A Literature Review." http://www.goldenpaints.com/conservation/conservation.pdf (accessed May 2010).

Learner, T. 2004. *Analysis of Modern Paints*. Los Angeles: The Getty Conservation Institute.

Ormsby, B., E. Kampasakali, C. Miliani, and T. Lerner. 2009. An FTIR-Based Exploration of the Effects of Wet Cleaning Treatments on Artists' Acrylic Paint Films. *e-Preservation Science*, 6:186–195.

Ormsby, B., T. Learner, G. Foster, J. Druzik, and M. Schilling. 2007. "Wet Cleaning Acrylic Emulsion Paint Films: An Evaluation of Physical, Chemical, and Optical Changes." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. Krueger, and M. Schilling, pp. 189–200. Los Angeles: The Getty Conservation Institute.

Ormsby, B., and P. Smithen. 2008. "A Scientific Evaluation of Surface Cleaning Acrylic Emulsion Paintings." In *Preprints. ICOM-CC 15th Triennial Conference New Delhi*, ed. J. Bridgeland, pp. 865–873. New Delhi: Allied Publishers.

Phenix, A., T. J. S. Learner, M. H. Keefe, and B. Ormsby. In press. "Evaluation of Cleaning Agents for Artists' Acrylic Paints with the Aid of High-Throughput (HTP) Testing." In *38th AIC Annual Meeting, Paintings Specialty Group*. Milwaukee, Wis.

Smith, G. 2007. "Aging Characteristics of a Contemporary Acrylic Emulsion Used in Artists' Paints." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. Krueger, and M. Schilling, pp. 236–246. Los Angeles: The Getty Conservation Institute.

Stavroudis, C., and T. Doherty. 2007. A Novel Approach to Cleaning II: Extending the Modular Cleaning Program to Solvent Gels and Free Solvents, Part 1. *WAAC Newsletter*, 29(3):9–15.

Stavroudis, C., T. Doherty, and R. Wolbers. 2005. A New Approach to Cleaning I: Using Mixtures of Concentrated Stock Solutions and a Database to Arrive at an Optimal Aqueous Cleaning System. *WAAC Newsletter*, 27(2):17–28.

Stulik, D., and R. Wolbers. 2004. "Project Outcome, Spin-offs, and Future Research." In *Solvent Gels for the Cleaning of Works of Art: The Residue Question*, ed. V. Dorge, pp. 131–144. Los Angeles: The Getty Conservation Institute.

Wolbers, R. 2000. *Cleaning Painted Surfaces: Aqueous Methods*. London: Archetype Publications.

Zumbühl, S., F. Attanasio, N. Scherrer, W. Müller, N. Fenners, and W. Caseri. 2007. "Solvent Action on Dispersion Paint Systems and the Influence on the Morphology—Changes and Destruction of the Latex Microstructure." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. Krueger, and M. Schilling, pp. 257–268. Los Angeles: The Getty Conservation Institute.

Cleaning of Acrylic Emulsion Paints: Preliminary Extractive Studies with Two Commercial Paint Systems

Richard Wolbers, Amanda Norbutus, and Anthony Lagalante

ABSTRACT. There has been a steadily growing body of literature within the conservation research community specifically designed to evaluate the impact of solvents, including water, on both swelling and extraction of acrylic dispersion paint film used in fine art applications. Water and other solvent conditions tested thus far on these acrylic paint films have tended to extract significant, measurable quantities of paint film components, supporting the idea that both traditional easel painting aqueous and solvent cleaning and coating strategies for conserving paintings and painted artifacts that carry these types of paints will severely compromise these materials. To date, only a very limited number of aqueous conditions have been tested, however. In this paper the results of a series of experiments specifically designed to look at pH and conductivity effects of cleaning solutions on acrylic paints are reported. Specifically, Golden Artist Colors' Heavy Body Tube Colors (New Berlin, New York) and ColArt's USA Liquitex Acrylic Tube Colors (Piscataway Township, New Jersey) were used as the model test paints. Both digital microscopy and liquid chromatography–mass spectrometry were used to characterize the physical changes in these paints in terms of surface area increases and to quantify the surfactant moieties extracted. Results from preliminary extraction experiments suggest that there are clear trends in the swelling of these paint films under short-term immersion conditions as a function of pH and conductivity in the presence of monovalent ions.

INTRODUCTION

After World War II, a revolution in visual artistic media using waterborne emulsion polymer paints occurred. The broad, even fields of color associated with iconic Pop artists like Warhol, Lichtenstein, and Hockney; the hard-edged geometric minimalism of artists like Kenneth Noland and Frank Stella; and the wash, or "stain," paintings of color field artists like Frankenthaler, Francis, and Olitski were now all possible with these new paints (Crook and Learner, 2000). The ability of these paints to be used as incredibly transparent water washes and, at the other extreme, as heavy-bodied dense gel-like materials enabled artists to accomplish things visually that were not possible previously with slower-drying oil-based paint media. But the "revolution" was a two-edged sword: on the one hand, this new media enabled artists to move aesthetically far from the traditional limitations of oil paints; on the other hand, it ironically has left us with a cultural legacy replete with some of the greatest challenges in terms of conserving and exhibiting these treasures. Whereas cultural heritage scientists have had over five hundred years to develop conservation materials and methods for treating and exhibiting traditional oil paintings, the same cannot be said for paintings created in emulsion polymer paints.

***Richard Wolbers**, Art Conservation Program, University of Delaware, Conservation Division, 5105 Old Kennett Pike, Winterthur, Delaware 19735, USA. **Amanda Norbutus**, Preservation Studies Program, University of Delaware, 5105 Old Kennett Pike, Winterthur, Delaware 19735, USA. **Anthony Lagalante**, Chemistry Department, Villanova University, Villanova, Pennsylvania 19085, USA. Correspondence: Richard Wolbers, atwolbers@earthlink.net.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

The first acrylic-based paintings were accessioned into museum collections a little over 50 years ago, and their numbers in major public institutions have grown almost exponentially since then. To say that these artworks represent a significant cultural asset would be an understatement, both in terms of their sheer monetary value and from the standpoint of their social, economic, and cultural significance. Methods for cleaning (removing accumulated soils) and protecting traditional oil paintings (coatings) used on contemporary artworks can significantly damage and alter their appearance, and fundamental research into new, more appropriate conservation methods and materials characterization has just begun within the last decade or so.

Modern paint conservation issues in museums are exacerbated when these same waterborne emulsion polymer paints are used in outdoor public murals. The international popularity of public murals rocketed soon after one of the first modern public murals debuted in Chicago in 1969 (William Walker's *Wall of Respect*). Walker's spontaneous form of expression inspired many artists to create community murals (Levick and Young, 1988). Murals number in the thousands in cities such as Los Angeles, Philadelphia, Chicago, Atlanta, Boston, Paris, Dublin, and London. Murals today are in danger of being irreversibly damaged or lost if they are not properly protected from the chemical, mechanical, and physical stresses of everyday exposure (e.g., neglect, graffiti, ultraviolet radiation, pollution, and windblown sand, salt, and dirt; Garfinkle, 2003:12; Golden, 2003:4). No other art form is so *accessible* to the public, and subsequently, no other art form is so *exposed* and *susceptible* to the elements, aging, and vandalism (Drescher, 2003:5). Initially, most murals were painted in urban neighborhoods with inexpensive materials; the muralists were highly experimental in formulating their techniques (Becker, 2002; Graves, 2007; Shank and Norris, 2008). This has resulted in many poorly crafted murals that diminish in appearance rather than providing a strong, well-defined image for a community (Figure 1). Although the development of modern synthetic paints allowed artists to paint bold, bright, affordable murals for the enjoyment of all, the widespread use of this modern paint has introduced new preservation concerns for the next generation of cultural heritage scientists. The future of murals now resides in the hands of the

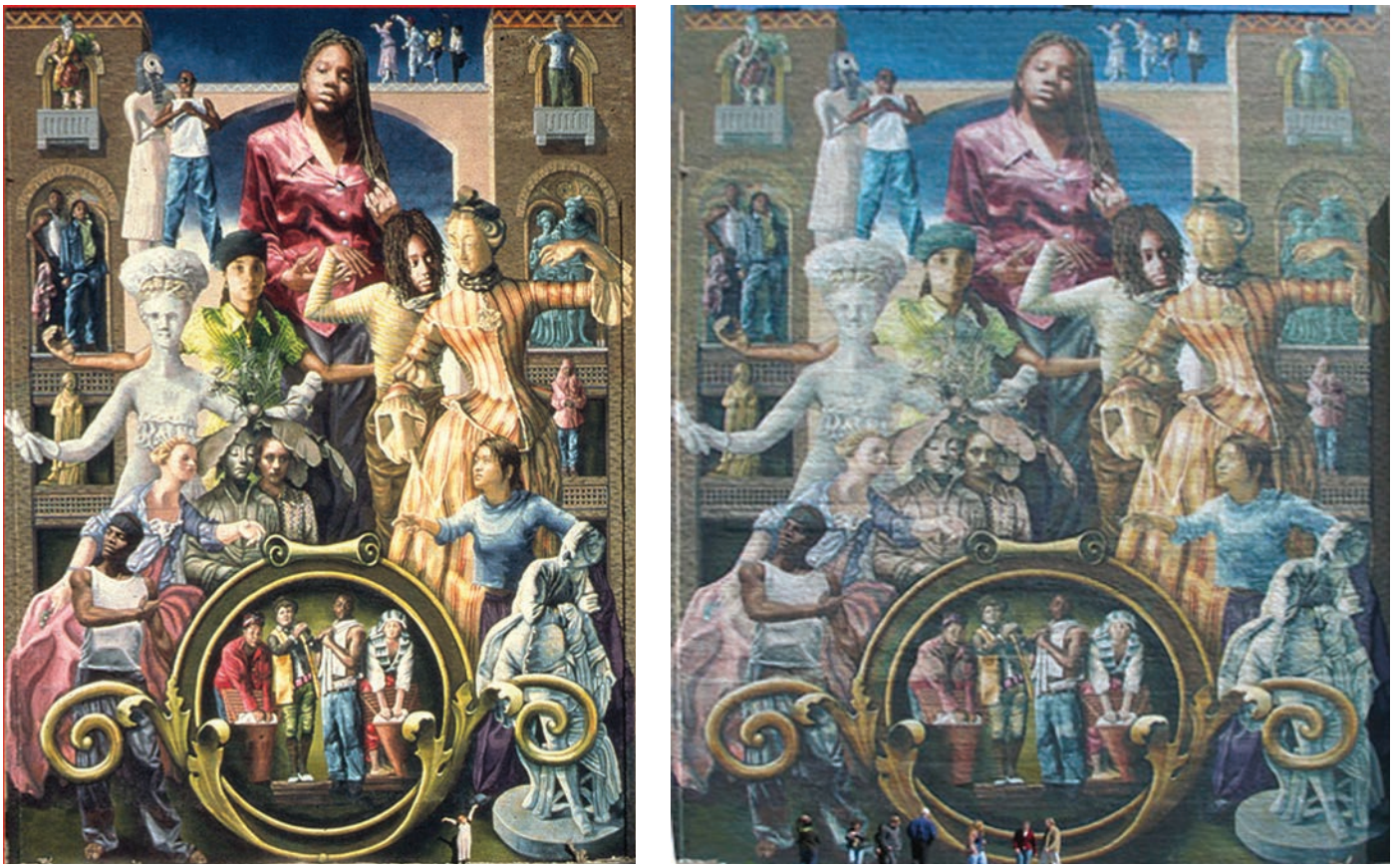


FIGURE 1. The *Common Threads* mural in Philadelphia by local artist Meg Saligman is an example of rapid deterioration due to pigment changes. The earlier photograph, from 1997, is from http://www.muralfarm.org; the later photograph, from 2005, is courtesy of Joyce Hill Stoner.

advocates of public murals, the muralists who continue to paint them, and the conservators and scientists who are acting to save endangered murals while researching materials and methods to retard degradation and further loss.

Jablonski et al. (2003) presented what has now become a pivotal comprehensive review of both the complicated array of materials found in modern artists' acrylic emulsion paints and the host of concerns expressed by surveyed conservators over the potential conservation problems inherent in these complex painting materials. Important concerns included (1) paint film swelling and (2) the extraction of paint film components. Either or both of these effects may possibly alter the long-term mechanical or bulk properties or compromise aesthetically the appearance (color, gloss, adhesion) of the paint surfaces. The low glass transition temperature T_g values of the bulk paint polymers (earlier, poly ethyl acrylate methyl methacrylate [EA/MMA] copolymers and, more recently, poly butyl acrylate methyl methacrylate [BA/MMA] copolymers) and empirical experience with these films suggested that their lack of hardness at normal ambient temperatures, along with a tendency to segregate or separate surfactant materials to their surfaces, created a markedly soft surface that is likely to entrain soils. Empirical experience indicates that pure water and nearly all solvent applications to acrylic paint films exacerbates the extraction of paint surfactants, swells or softens the paints, and therefore severely limits the range of surface treatment or cleaning options. Solvent and water absorption and swelling of artists' acrylic paint films are a function of a number of factors, including the type and amount of materials present within these films (the compositions of which may vary from decade to decade and from manufacturer to manufacturer) and the physical arrangement of materials within these films. Pigment loading, fillers, age hardening at surfaces, polymer elasticity (T_g and copolymer ratio), film drying rate and dynamics, film thickness, priming or support layers beneath the acrylic films, transport of solvents and water through these films, prior treatment, and environmental factors (prior extractions, length of aging, RH, and temperature fluctuations) may all influence absorption and swelling phenomena in these films (Ormsby and Learner, 2009).

Zumbühl et al. (2007) found that the highest acrylic film swelling occurred in chlorinated and aromatic solvents and the least swelling occurred in nonpolar solvents, such as aliphatic hydrocarbons. Solvent effects were also shown to extend well into the tested films. After freeze fracturing to reveal cross sections of treated test films, samples were examined with scanning electron microscopy, and the "cellular" morphology of partially coalesced micelles within the paint films were also seen to be highly disrupted. Here scale may be critical; even small surface disruptions have been reported on acrylic paint surfaces that were exposed to hydrocarbon solvents (Snuparek, 1972). The Zumbühl et al. study was limited to solvent testing only and not aqueous cleaning conditions per se; nonetheless, this study provides a useful, adaptable model for conducting swelling-related experiments on test paint film samples and highlights their limitations to date. Swelling phenomena, however, have been extrapolated from 2-D images captured to this point. The imaging of swollen and unswollen paint surfaces on a *macroscale* has primarily been investigated using wide-field optical microscopy and, in a single study, laser scanning 3-D profilometry (Eipper, 2005; Eipper and Frankowski, 2007). Scanning electron microscopy and atomic force microscopy images have recorded morphological changes in the surface features of these films on a nanoscale after solvent (including hydrocarbon solvents) and water exposures (Ormsby et al., 2007a; Ploeger et al., 2007). Increases in pores or perforations, surface erosion, roughness, displaced materials, scratches, etc., have also been reported qualitatively (Eipper and Frankowski, 2007).

Likewise, several groups have confirmed the swelling of artists' acrylic paint films with pure water alone as a general solvent (Murray et al., 2001; Digney-Peer et al., 2004; Owen et al., 2004; Ploeger et al., 2005a; Ormsby et al., 2007a), but variations in pH and ionic strength have not been studied in any concerted fashion to this point. It is conceivable that the extraction of ionic materials may be slowed at isotonic or isoelectric conditions, but these types of films have not been fully tested in this regard. In extractive studies done thus far (Whitmore and Colaluca, 1995; Learner, 2004; Ploeger et al., 2005b; Scalarone et al., 2005; Smith, 2005, 2007; Ormsby et al., 2006, 2007b; Chiantore and Scalarone, 2007) the primary segregated materials on artists' acrylic paint surfaces have been nonionic structures. Triton X-405 and X-305 (Ormsby et al., 2007b, 2008a, 2008b; Hoogland and Boon, 2009a, 2009b) have been identified in swabs taken from the surface of acrylic paintings; this is consistent with known industry-wide formulation practice for these paints (Croll, 2007). Additional minor amounts of paint film constituents have also been found with aqueous extraction methods; these include minor amounts of pigments, fillers, inorganic soil aerosols such as silicates and $CaSO_4$, residual acrylic polymer, thickeners such as hydroxyethyl cellulose (HEC), coalescing agents such as Tamol 371, common preservatives such as Dowicil 75, hydrotropes such as Triton CF-10, and other trace surfactant structures (Ormsby and Learner, 2009). The amounts of materials extracted have been quantified in some cases and range from 0.5% to 18% of the overall dry paint film weight (Whitmore et al., 1996; Learner et al., 2002; Digney-Peer et al., 2004; Ploeger et al., 2005a; Hayes et al., 2007; Ormsby et al., 2008b). Extraction kinetics indicate that relatively high percentages of the extracted materials are lost within the first 15 minutes of extraction and seem to approach a maximum in 24 hours in most cases.

The approach in the present study has been to initially examine further the notion of water sensitivity in these paints by testing both the physical swelling and the concomitant extraction of the most prevalent extractable material (nonionic surfactant) by subjecting test films to both varied pH and ionic strength compositions. Aqueous cleaning systems still represent the least toxic and most green, VOC-compliant methods available at present to conservators. Our initial premise was that given the likely paint film components, swelling, and therefore (at least some) extraction, of paint film materials must be a function of

and can be mitigated by aqueous solution properties such as pH and ionic strength. We decided to work with a limited, manageable sampling of paints from two commercially available artists' paint systems currently available to mural artists to measure their swelling response using 3-D digital imaging techniques, along with liquid chromatography–mass spectrometry (LC-MS) to quantify the amount and type of surfactant extracted under all of the conditions tested.

MATERIALS AND METHODS

Sample Preparation

Paint samples were drawn from two commercial systems (see Table 1). The paints were cast into essentially two formats: a microdot array directly on borosilicate slide and continuous films, as drawdowns, on silicone-treated Mylar sheets.

The microdot arrays were created using a Performus III (Nordson/EFD) microdispenser (10 mL syringe barrel, PN 7012114, and an EFD precision tip, PN 7018417) under a nitrogen head to apply uniformly 5 μL volume wet samples (160 μg dry) of unmodified paint onto clean standard (25 × 75 mm) borosilicate glass slides. A Velmex stage (XN-0040-M0-71) and stepping controller (PK 245-01AA) were used to secure and move the microdot slides under the application head in a predefined grid pattern. Paint microdots were applied in a manner so that they were grouped together in arrays of 4 paint sample dots in 16 rectilinear 7 × 7 mm areas (Figure 2). After drying, a ProPlate Multi-Array Slide System (Grace Bio-Labs) frame could be overlaid on the individual microdot slides to create 16 well-defined and self-contained treatment wells surrounding each group of four paint dots. Four of these frames (and their concomitant glass slides) conveniently fit into a larger frame in a standard 96 well microtiter plate (80 × 120 mm) format, allowing for the creation of 64 discrete test wells (300 μL/well volume) altogether. The microdot samples were used for the 3-D digital imaging experiments.

The continuous drawdown samples were prepared using a glass knife. The paint samples were used directly from the commercial tubes and spread uniformly into thin rectangular layers

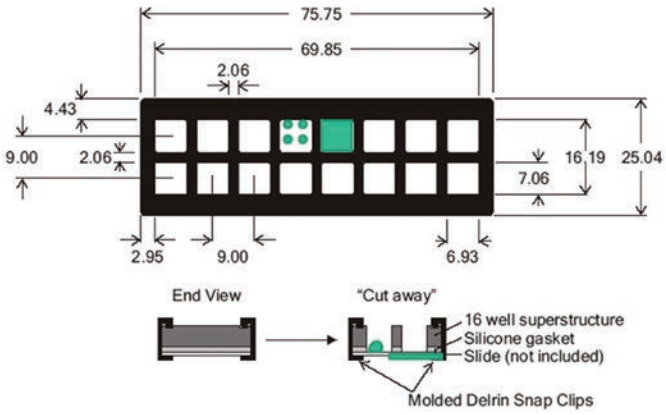


FIGURE 2. Illustration of acrylic dot arrays and the ProPlate Multi-Array Slide System for creation of individual treatment wells.

with the glass knife edge on a Mylar-covered surface using two parallel aluminum plates (0.80 mm thickness) as guides to create 20 × 40 cm wet films. After drying, 25 × 75 mm strips were cut from the dried drawdown films and overlaid on standard borosilicate microscope slides. The ProPlate Multi-Array Slide system frames were applied over these slide-supported films to again create 16 discrete test wells/paint sample of *continuous* dry paint films (each 7 × 7 mm well was equivalent to 49 mm^2 surface area that could be extracted and approximately 13–15 mg total weight of paint). The continuous-film samples were used for extraction and the LC-MS/MS experiments. All paint sample types were dried for a minimum of 4 months in a dust-free, dark enclosure prior to testing.

A standard array of 64 buffered and ionically adjusted solutions was applied to both paint sample types (mounted in the ProPlate Multi-Array frames) for standard 15 minute contact times. These solutions were prepared from Sigma-Aldrich reagents and using citric acid (pK_a 3.13, 4.76, 6.40), triethanolamine (TEA, pK_a 7.9), and diethanolamine (DEA, pK_a 9.2). The pH of 2 L of a 0.5% solution of citric acid was raised incrementally using either TEA or DEA to create stock buffered solutions at a pH of

TABLE 1. Manufacturers, colors, and identification of the paint samples used in this study.

Hue	Golden Acrylic Colors Heavy Body	ColArts Liquitex Heavy Bodied Acrylic
Black	1200 iron oxide PBk11	276 iron oxide PBk11
White	1380 titanium dioxide PW6	432 titanium dioxide PW6
Red	1210 naphthol AS-D PR112, 1277 pyrrole red PR254	292 naphthol carbamide PR170
Yellow	1120 cadmium zinc sulfide PY35	160 cadmium zinc sulfide PY35
Blue	1400 polysulfide of sodium-alumino-silicate PB29, 1140 cobalt blue PB28	382 complex silicate of sodium and aluminum with sulfur PB 29
Green	1270 chlorinated copper phthalocyanine PG7	317 chlorinated copper phthalocyanine PG7

2.5, 3.5, 4.5, 5.5, 6.5, 7.5, 8.5, and 9.5. The conductivity of each stock solution was adjusted to 6.0 mS using a 1 M NaCl solution and a calibrated Horiba B-167 portable conductivity meter. Aliquots from each adjusted stock solution were removed and either diluted with deionized water to create standard solutions at 0.6 mS (pH 2.5–9.5) or adjusted with additional amounts of 1 M NaCl solution to increase the conductivities to 16, 26, 36, 46, 56, and 66 mS (again, all at pH of 2.5–9.5). The 64 citrate, TEA, and DEA solutions thus created varied in pH from 2.5 to 9.5 and in conductivities from 0.6 to 66 mS overall.

Digital Imaging

One hundred microliters of each of the 64 aqueous test solutions were applied to the microdot paint samples, and images were collected after 15 minutes of contact time with the buffered, ionically adjusted test solutions in situ. Digital images were acquired with a Hirox KH7700 digital microscope equipped with a MX (G)-5040Z (50×) lens (3.87 μm resolution), using the proprietary Hirox acquisition software. Digital files were further processed using Image-Pro Plus to calculate surface areas. The 2-D and 3-D surface plots were constructed and expressed as percentage increase in surface area from the initial surface area for each sample (see Figure 3a–e).

LC-MS/MS

Supernatants from each well of the continuous-film samples were aspirated off and set aside for LC-MS/MS after 15 minutes of contact time for characterization of aqueous extractable materials. The supernatants (~100 μL) were characterized by LC-MS/MS using a Shimadzu Prominence HPLC interfaced with an Applied Biosystems 3200 QTRAP (VU).

Preliminary testing had suggested that in the ColArts Liquitex paints, an A_{16-18} EO [23] surfactant was present (a 16–18 carbon alkyl polyethoxylate structure with an average of 23

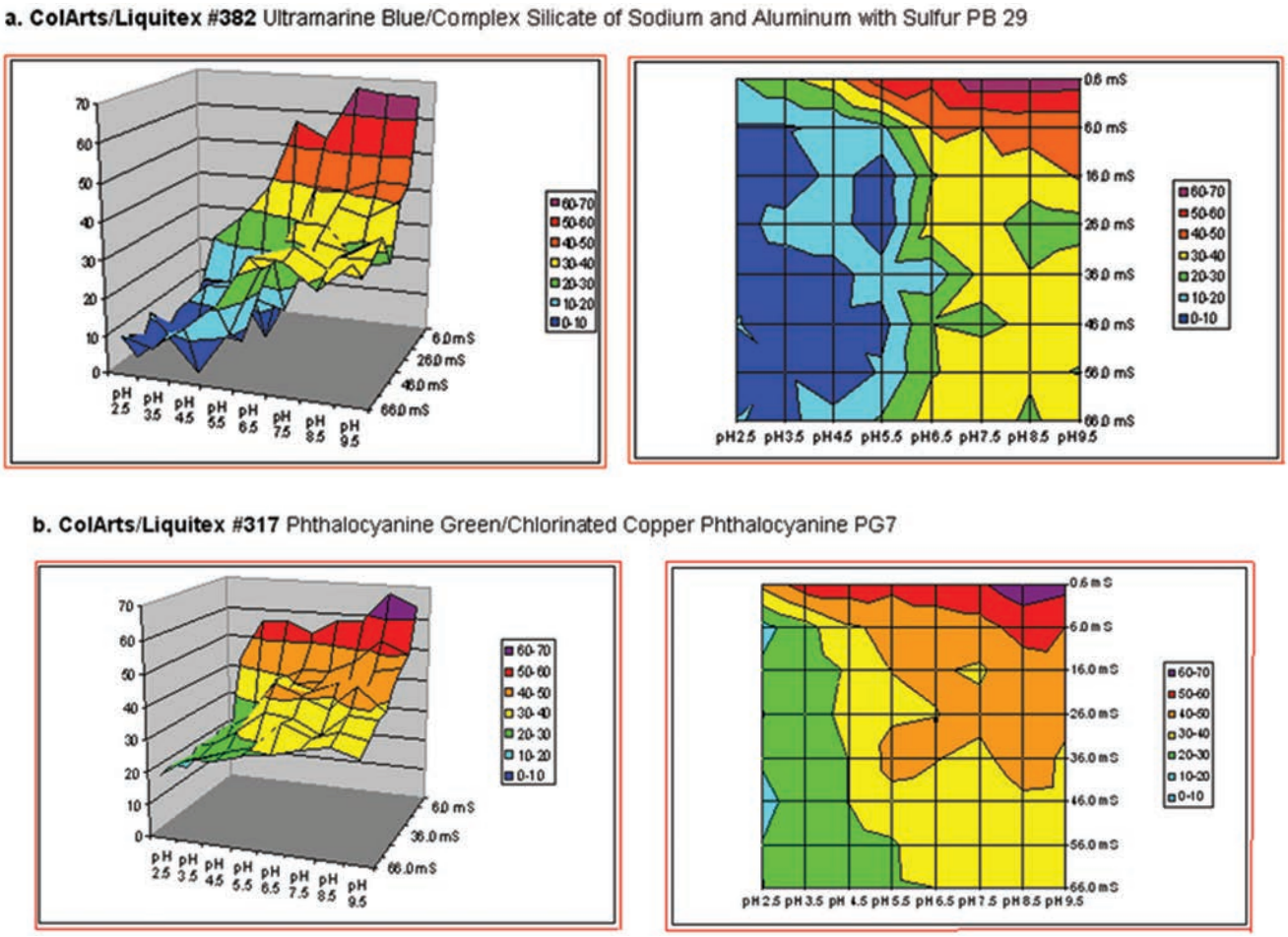
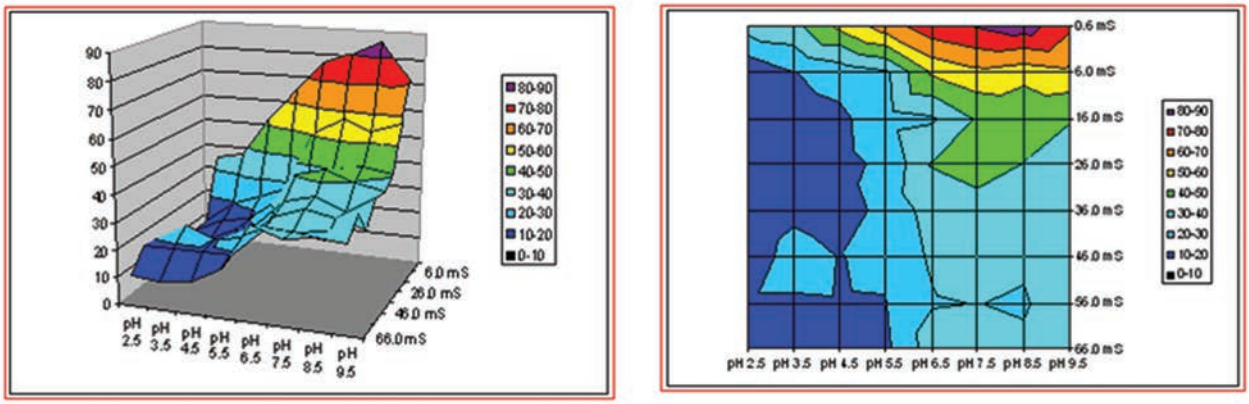
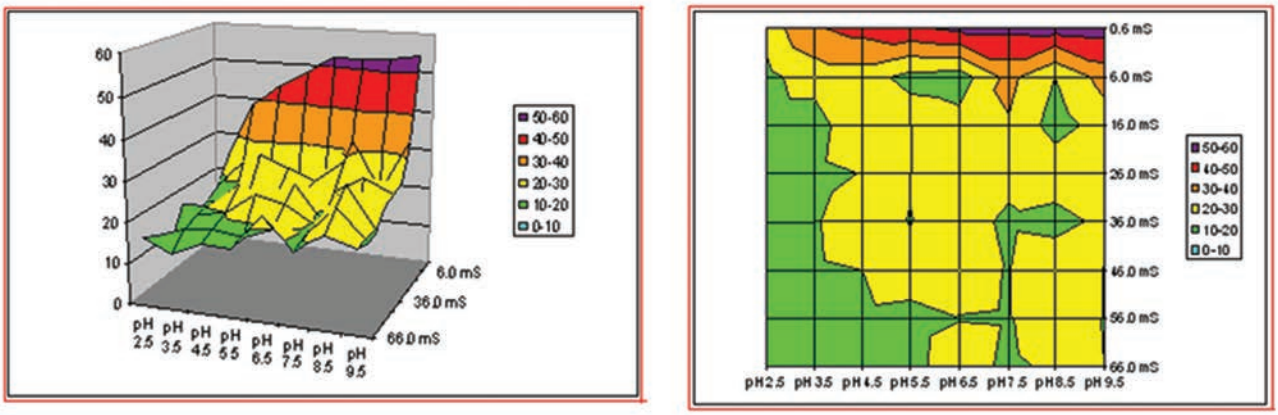


FIGURE 3. Percent (%) surface area increase on swelling ColArts Liquitex samples after 15 minutes of contact time with different buffers at different ionic strengths. (*continued*)

c. ColArts/Liquitex #276 Mars Black/Iron Oxide PBk11



d. ColArts/Liquitex #160 Cadmium Yellow Light/Cadmium Zinc Sulfide PY35



e. ColArts/Liquitex #432 Titanium White /Titanium Dioxide PW6

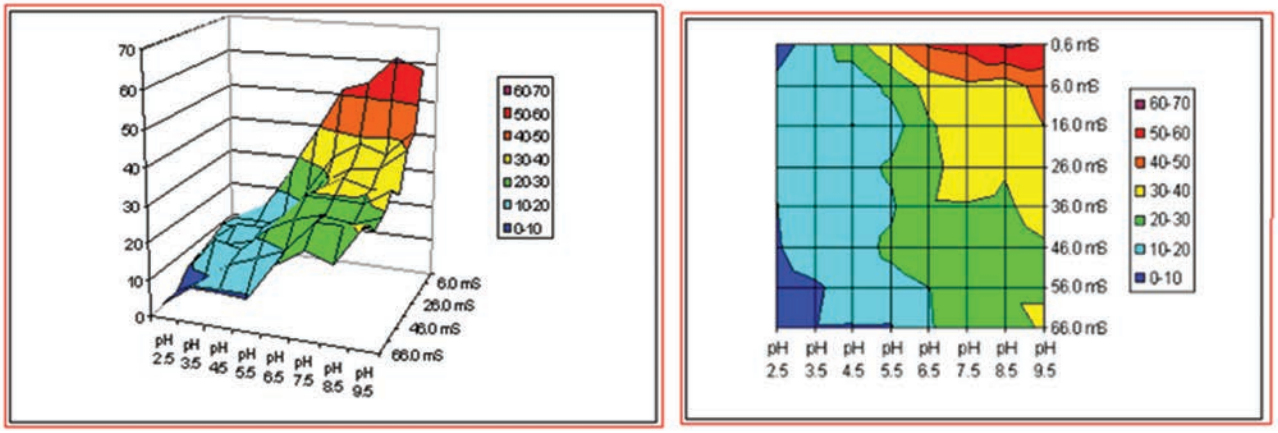


FIGURE 3. (*continued*) Percent (%) surface area increase on swelling ColArts Liquitex samples after 15 minutes of contact time with different buffers at different ionic strengths.

ethoxylate units in length), but no standard reference material identical to the suggested structure was found. In the Golden Artist Colors (GAC) paints, Triton X-305 (a 6–9 carbon aliphatic phenoxy polyethoxylate structure with an average of 30 ethoxylate units, A_{6-9} Phenoxy-EO [30]) was found to be the predominant surfactant. The Triton X-305 was obtained as a standard material and was quantified by ESI+ ionization (Electrospray Ionization in the Positive ion mode) using $[M+NH_4]^+$ precursor ions (Loyo-Rosales et al., 2003; Jonkers et al., 2005). The Triton X-305 A_{8-9}Phenoxy-EO_n moieties were initially separated on a reversed-phase C_{18} column, with optimized mass reaction monitoring (MRM) transitions (tandem MS techniques have on-column limits of detection approximately 0.1–1 pg; Houde et al., 2002; Loyo-Rosales et al., 2003). Hybrid QqQ_{LIT} geometry (hybrid triple quadruple/linear ion trap) mass analyzers have been successful in identifying alkylphenoxy polyethoxylate (APEO) degradation products in the environment because of the ability of the linear ion trap (LIT) to record enhanced product ion scans (Frömel and Knepper, 2008), and they have provided a useful technique in this instance for the identification and speciation of the surfactants in both commercial acrylic paint formulations. The use of precursor ion and neutral loss scans were used to generate criteria for subsequent LIT scans using an information dependent acquisition in the Analyst software. The LIT triggered scans were used to provide a means to identify degradation or proprietary formulation ingredients in the surface extract. Preliminary experiments on Triton X-305 had suggested that ammonium-buffered mobile phases were preferred and MS-MS fragmentation on ammonium adducts produced the expected ethoxylate and phenol ethoxylate product ions (Loyo-Rosales et al., 2003) and allowed for the selective multiple MRM identification of expected APEOs with specific EO chain lengths. Additionally, the use of the LIT enhanced multicharge scan functions provided a unique detection capability for doubly charged ammonium adducts. The MRM product ions were quantified against a standard dilution curve of the Triton X-305 and were expressed normalized to the highest product ion (Figures 4 and 5) as color-coded surface plots in both three and two dimensions for all 64 of the aqueous test conditions.

RESULTS AND DISCUSSION

The collection of physical swelling data is still ongoing, but it was clear thus far that although there were no combinations of pH and conductivity in solution where swelling was eliminated, there were distinct trends that seemed to emerge from the data (see Figure 3a–e). In the Liquitex samples tested, for instance, there were sharp increases in surface area below about 6 mS conductivity, as well as sharp increases above a pH of about 6. The former is probably due to an osmotic-like effect; at conductivities below the isotonic point in these films swelling is rapid. This is equivalent to a *hypotonic* solution (in osmosis), and there should be a swelling of the film and a concomitant loss of film materials like surfactant (and this, indeed, appears to be the case; see Figure 3). This is an especially important observation, given the all too frequent studio practice of fine art conservators to initially clean these surfaces with deionized water. It also suggests a primary mechanism for loss of film integrity in mural paintings in the environment at large because they are subject to constant washing with rainwater. It is worth noting that the same dramatic swelling effect (at least after the 15 minute test interval) does not occur at high conductivities. This would be equivalent to a *hypertonic* solution (in osmosis), and there should be, if anything, a shrinking of the film that would cause less film materials, such as surfactants, to leave the film as readily. Again, there is some suggestion of this effect in the Figure 3 plots.

Presumably, diffusion of ionic material in solution into the swollen paint films is a much less pronounced phenomenon than the swelling at low conductivities through osmotic pressure. Longer contact times might clearly delineate the isotonic point on these films, however.

In the Liquitex films tested there appears to be a distinct increase in swelling above a pH of 6. The nominal pK_a of polyacrylic acid moieties can be this high (6.3), and it may be that the sharp rise in swelling at or around a pH of 6 is simply a reflection of the increased ionization of polyacidic materials like polyacrylic acid, which are used in these films as both thickeners and pigment dispersal aids. Both partially hydrolyzed and neutralized poly co-maleic anhydride/isobutylene (Tamol 371) and Primal ASE-60 (sodium polyacrylic acid) or similar materials have been isolated from these types of paints and may account for the observed pH-dependent rise in swelling in this pH range. Characterizing and titrating the exact polyacidic materials in the Liquitex films may help to determine if this is true.

The extraction data for GAC collected thus have yielded limited useful information. Some of the tested paints simply did not appear to contain or be manufactured with Triton X-305, and their surfactant system(s) will need to be further characterized. The paints that were tested and that did contain Triton X-305 (A_{8-9} PEO [30]) were quantified with LC-MS/MS, and some (see Figure 4a–c), notably the GAC phthalocyanine green (color 1270, PG7) and cobalt blue (color 1140), did seem to exhibit minimal surfactant extractions that were conductivity dependent, that is, between 16 and 26 mS, at all pHs. In the case of GAC pyrrole red (color 1277, PR254) this was reversed; however, the highest extraction of the surfactant was around 26 mS and generally at most pHs. The solubility phenomena associated with nonionic structures is complex, however. The EO chain length as well as the hydrocarbon-to-EO ratio can determine the solubility of these materials in water. Both H^+ and monovalent ions like Na^+ can increase cloud point temperatures T_{cp} and hence the solubility of these materials in aqueous solutions. In the case of both the phthalocyanine green and the cobalt blue paints, it is clear that at both high and low conductivities their solubility seemed to increase slightly.

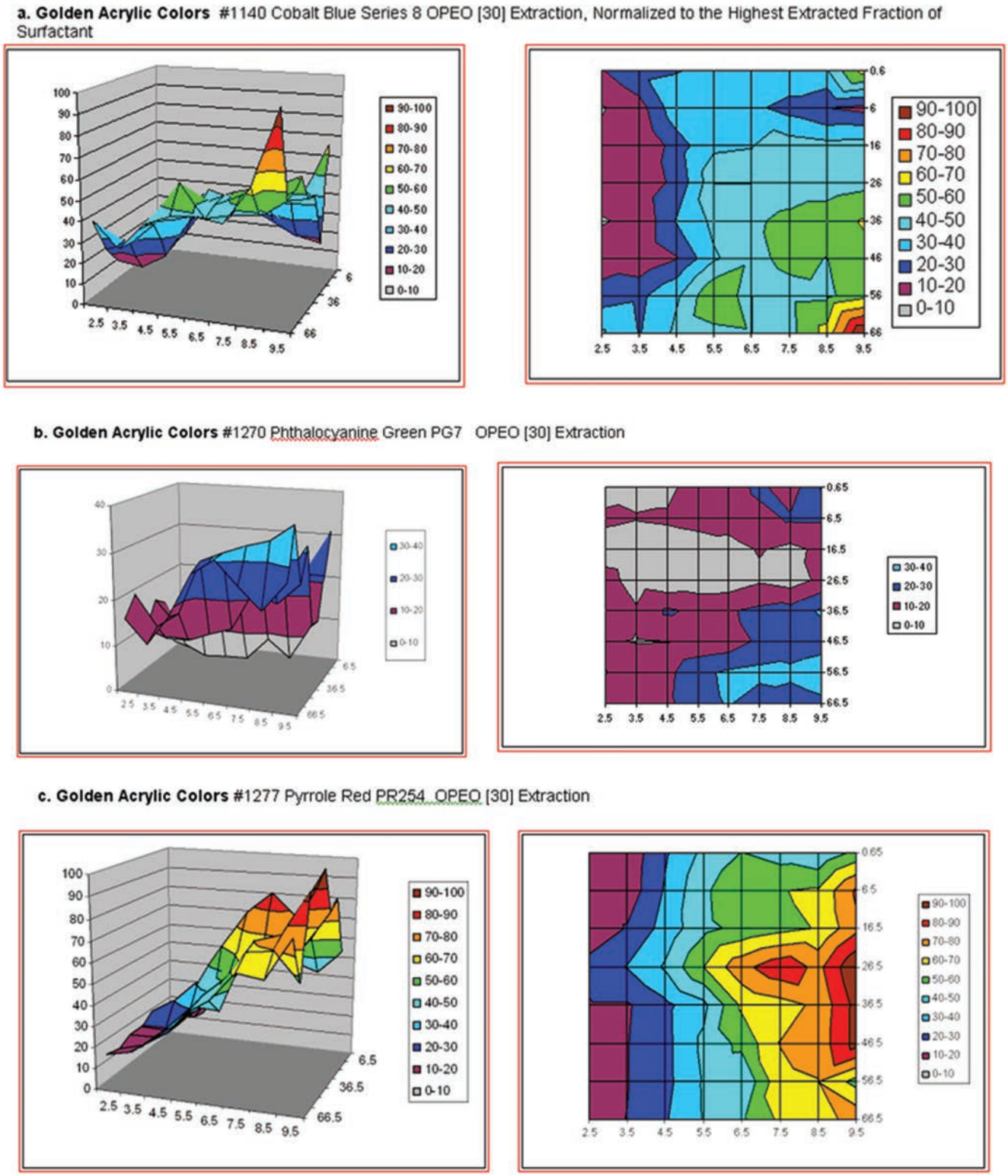


FIGURE 4. A-phenoxyOPEO[30] extraction from Golden Artists Colors paint after 15 minutes of contact time with the prepared solutions and normalized to the highest extracted fraction of surfactant.

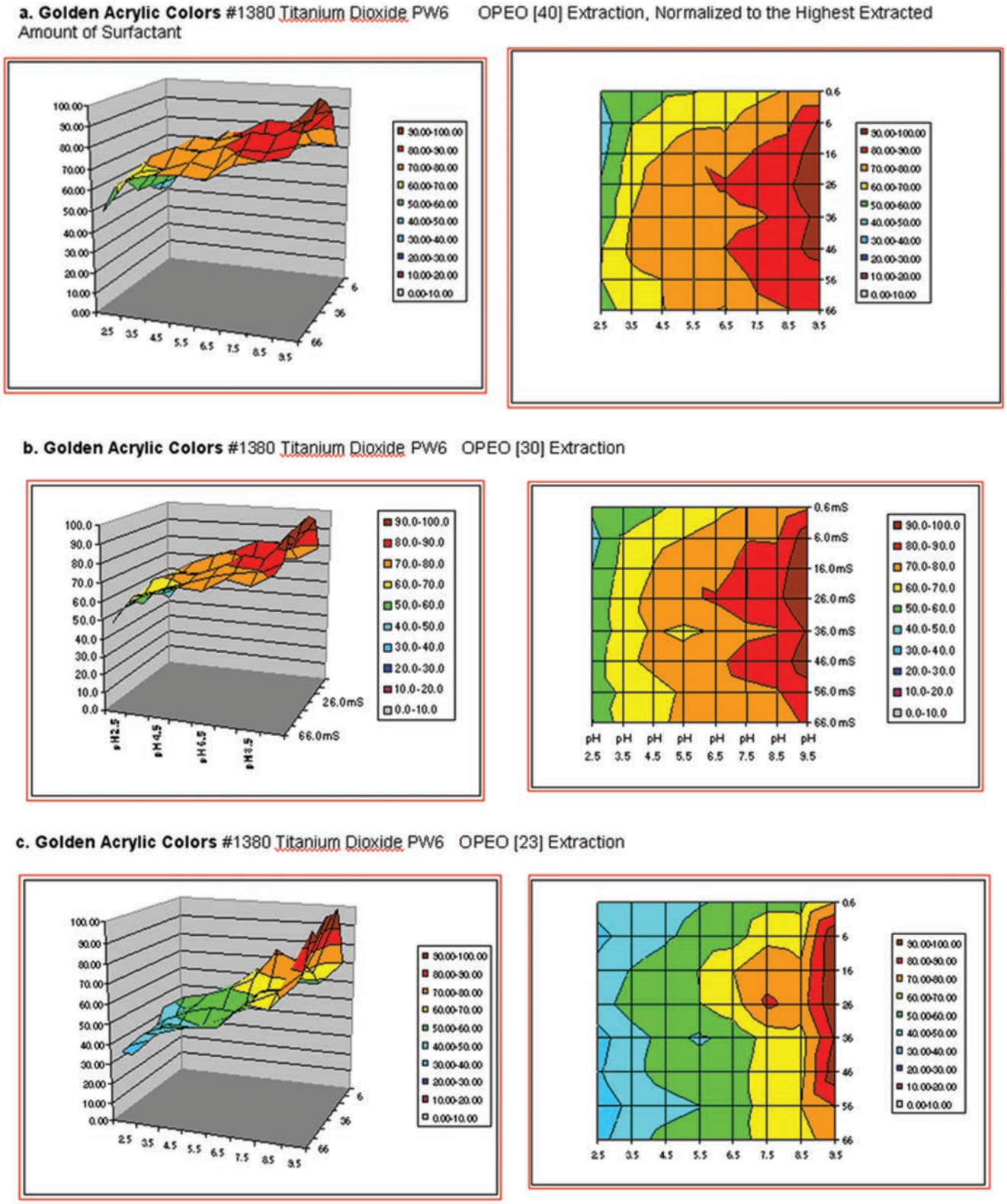


FIGURE 5. Golden Artists Colors titanium dioxide OPEO[n] speciation, normalized to the highest amount of surfactant extracted.

It is clear as well that at all aqueous conditions tested surfactant is solubilized, but the pattern of extraction does not necessarily follow that of the physical swelling data. It also remains to be seen if this is actually surface-segregated material, leached material, or a combination of both being solubilized.

When MRM experiments were performed on one paint sample in particular (GAC titanium dioxide, color 1380, PW6; Figure 5a–c), there was a clear speciation effect of the surfactant solubility as a function of pH. In all cases, there appeared to be an *increase* in surfactant extraction as pH went up. When the amounts of APEO [23], APEO [30], and APEO [40] species in particular were compared, however, in the extracted supernatants, *more* surfactant was extracted as the [EO] chain length increased at any given pH. Thus, as [EO] length increases, so too does its role in solubilizing the overall surfactant molecule apparently. The longer the [EO] moiety is, the more pronounced the effects of small ions like H+ and Na+ are in solution with the surfactant. This is especially noteworthy in that one of the likely deterioration pathways for AEO and APEO surfactant structures is through the gradual loss of the [EO] chains as low molecular weight volatile fragments, resulting in the eventual accrual of the parent fatty alcohol or alkyl phenol on these surfaces as a natural consequence of aging and exposure. As the [EO] chain is lost incrementally, the solubility of the AEOs or APEOs also gradually increases in the polymer films, and their tendency to segregate or exude from the film may diminish with time as well. The other practical ramification of this observation may be that well-aged or exposed paint films may tolerate higher-pH aqueous systems as their constituent surfactants break down with exposure.

REFERENCES

Becker, H. 2002. *Art for the People: The Rediscovery and Preservation of Progressive- and WPA-Era Murals in the Chicago Public Schools 1904–1943*. San Francisco: Chronicle Books.

Chiantore, O., and D. Scalarone, 2007. "The Macro- and Micro-assessment of Physical and Aging Properties in Modern Paints." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. W. Krueger, and M. R. Schilling, pp. 96–104. Los Angeles: The Getty Conservation Institute.

Croll, S. 2007. "Overview of Developments in the Paint Industry since 1930." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. W. Krueger, and M. R. Schilling, pp. 17–29. Los Angeles: The Getty Conservation Institute.

Crook, J., and T. Learner. 2000. *The Impact of Modern Paints*. London: Tate Gallery Publishing.

Digney-Peer, S., A. Burnstock, T. Learner, H. Khanjian, F. Hoogland, and J. J. Boon. 2004. "The Migration of Surfactants in Acrylic Emulsion Paint Films." In *Modern Art, New Museums: Preprints to the IIC Bilbao Congress*, ed. A. Roy, and P. Smith, pp. 202–207. London: International Institute for Conservation.

Drescher, T. 2003. "Priorities in Conserving Community Murals." Paper presented at the Getty symposium "Mural Painting and Conservation in the Americas," Los Angeles, Calif., 16–17 May. http://www.getty.edu/conservation/publications/pdf_publications/ (accessed 15 November 2010).

Eipper, P. B. 2005. Acrylfarben-Oberflächenreinigung. [Acrylic Colors and Surface Cleaning.] *Museum aktuell,* 117:10–22.

Eipper, P. B., and G. Frankowski. 2007. "Examination of Cleaned Acrylic Paint Surfaces by 3D-Technology." In *Lasers in the Conservation of Artworks: Lacona VII : Program and Abstracts*, p. 204. Madrid: Consejo Superior de Investigaciones Científicas.

Frömel, T., and T. P. Knepper. 2008. Mass Spectrometry as an Indispensible Tool for Studies of Biodegradation of Surfactants. *Trends in Analytical Chemistry*, 27(11):1091–1106. http://dx.doi.org/10.1016/j.trac.2008.09.012.

Garfinkle, A. 2003. "The Legal and Ethical Consideration of Mural Conservation: Issues and Debates." Paper presented at the Getty symposium "Mural Painting and Conservation in the Americas," Los Angeles, Calif., 16–17 May. http://www.getty.edu/conservation/publications/pdf_publications/ (accessed 15 November 2010).

Golden, M. 2003. "Mural Paints: Current and Future Formulations." Paper presented at the Getty symposium "Mural Painting and Conservation in the Americas," Los Angeles, Calif., 16–17 May. http://www.getty.edu/conservation/publications/pdf_publications/ (accessed 15 November 2010).

Graves, K. 2007. An Investigation into the Technology and Behaviour of Contemporary Murals Executed on Portland Cement-Based Supports. M.A. diss., Courtauld Institute, London.

Hayes, J., M. Golden, and G. D. Smith. 2007. "From Formulation to Finished Product: Causes and Potential Cures for Conservation Concerns in Acrylic Emulsion Paints." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. W. Krueger, and M. R. Schilling, pp. 58–65. Los Angeles: The Getty Conservation Institute.

Hoogland, F. G., and J. J. Boon. 2009a. Development of MALDI-MS and Nano-ESI-MS Methodology for the Full Identification of Poly(ethylene glycol) Additives in Artists' Acrylic Paints. *International Journal of Mass Spectrometry*, 284:66–71. http://dx.doi.org/10.1016/j.ijms.2009.03.001.

———. 2009b. Analytical Mass Spectrometry of Poly(ethylene glycol) Additives in Artists' Acrylic Emulsion Media, Artists' Paints, and Microsamples from Acrylic Paintings Using MALDI-MS and Nano-ESI-MS. *International Journal of Mass Spectrometry*, 284:72–80. http://dx.doi.org/10.1016/j.ijms.2009.03.002.

Houde, F., C. DeBlois, and D. Berryman. 2002. Liquid Chromatographic–Tandem Mass Spectrometric Determination of Nonylphenol Polyethoxylates and Nonylphenol Carboxylic Acids in Surface Water. *Journal of Chromatography A*, 961:245–256. http://dx.doi.org/10.1016/S0021-9673(02)00661-1.

Jablonski, E., T. Learner, J. Hayes, and M. Golden. 2003. Conservation Concerns for Acrylic Emulsion Paints: A Literature Review. *Reviews in Conservation,* 4:3–12.

Jonkers, N., H. Govers, and P. De Voogt. 2005. Adduct Formation in LC-ESI-MS of Nonylphenol Ethoxylates: Mass Spectrometrical, Theoretical, and Quantitative Analytical Aspects. *Analytica Chimica Acta,* 531:217–228. http://dx.doi.org/10.1016/j.aca.2004.10.031.

Learner, T. 2004. *Analysis of Modern Paints*. Los Angeles: The Getty Conservation Institute.

Learner, T., O. Chiantore, and D. Scalarone. 2002. "Ageing Studies of Acrylic Emulsion Paints." In *Preprints ICOM-CC 13th Triennial Meeting, Rio de Janeiro*, ed. R. Vontobel, pp. 911–919. London: James and James.

Levick, M., and S. Young. 1988. *The Big Picture: Murals of Los Angeles*. London: Thames and Hudson.

Loyo-Rosales, J. E., I. Schmitz-Alfonzo, C. P. Rice, and A. Torrents. 2003. Analysis of Octyl- and Nonylphenol and Their Ethoxylates in Water and Sediments by Liquid Chromatography/Tandem Mass Spectrometry. *Analytical Chemistry,* 75:4811–4817. http://dx.doi.org/10.1021/ac0262762.

Murray, A., C. Contreras de Berenfeld, S. Y. Sue Chang, E. Jablonski, T. Klein, M. C. Riggs, E. C. Robertson, and W. M. A. Tse. 2001. "The Condition and Cleaning of Acrylic Emulsion Paintings." In *Materials Issues in Art and Archaeology VI,* ed. P. B. Vandiver, M. Goodway, J. R. Druzik, and J. L. Mass, pp. 1–8. Boston: Materials Research Society.

Ormsby, B., E. Hagan, P. Smithen, and T. Learner. 2008a. "Comparing Contemporary Titanium-White Based Acrylic Emulsion Grounds and Paints: Characterisation, Properties and Conservation." In *Preparation for Painting: The Artists' Choice and Its Consequences*, ed. J. H. Townsend, T. Doherty, G. Heydenreich, and J. Ridge, pp. 163–171. London: Archetype.

Ormsby, B., and T. Learner. 2009. The Effects of Wet Surface Cleaning Treatments on Acrylic Emulsion Artists' Paints. *Reviews in Conservation,* 10:29–41.

Ormsby, B., T. Learner, G. Foster, J. Druzik, and M. Schilling. 2007a. "Wet-Cleaning Acrylic Emulsion Paint Films: An Evaluation of Physical, Chemical and Optical Changes." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. Krueger, and M. Schilling, pp. 187–198. Los Angeles: The Getty Conservation Institute.

Ormsby, B., T. Learner, M. Schilling, J. Druzik, H. Khanjian, D. Carson, G. Foster, and M. Sloan. 2006. "The Effects of Surface Cleaning on Acrylic Emulsion Paintings—A Preliminary Investigation." In *Oberflächenreinigung: Materi-*

alien und Methoden [Surface Cleaning: Materials and Methods], ed. C. Weyer, pp. 135–149. VDR Schriftenreihe 2. Stuttgart, Germany: Theiss Verlag.

Ormsby, B., P. Smithen, F. Hoogland, T. Learner, and C. Miliani. 2008b. "A Scientific Investigation into the Surface Cleaning of Acrylic Emulsion Paintings." In *Preprints ICOM-CC 15th Triennial Conference, New Delhi,* ed. J. Bridgland II, pp. 857–865. New Delhi: Allied Publishers.

Ormsby, B., P. Smithen, and T. Learner. 2007b. "Translating Research into Practice—Evaluating the Surface Cleaning Treatment of an Acrylic Emulsion Painting by Jeremy Moon." In *Contemporary Collections,* ed. A. Paglierino and G. Osmond, pp. 97–109. Brisbane: Australian Institute for the Conservation of Cultural Materials.

Owen, L., R. Ploeger, and A. Murray. 2004. The Effects of Water Exposure on the Surface Characteristics of Acrylic Emulsion Paints. *Journal of the Canadian Association for Conservation,* 29:8–25.

Ploeger, R., A. Murray, S. Hesp, and D. Scalarone. 2005a. "An Investigation of the Chemical Changes of Artists' Acrylic Paint Films When Exposed to Water." In *Materials Issues in Art and Archaeology VII,* ed. P. B. Vandiver, J. L. Mass, and A. Murray, pp. 49–56. Warrendale, Pa.: Materials Research Society.

———. 2007. "Morphological Changes and Rates of Leaching of Water-Soluble Material from Artists' Acrylic Paint Films During Aqueous Immersions." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. Krueger, and M. Schilling, pp. 201–207. Los Angeles: The Getty Conservation Institute.

Ploeger, R., H. F. Shurvell, E. W. Hagan, and A. Murray. 2005b. "Infrared Analysis of Materials Leached by Water from Acrylic Paint Films." In *The Sixth Infrared and Raman Users Group Conference (IRUG6)*, ed. M. Picollo, pp. 46–51. Padua: Il prato.

Scalarone, D., O. Chiantore, and T. Learner. 2005. "Ageing Studies of Acrylic Emulsion Paints. Part II. Comparing Formulations with Poly(EA-co-MMA) and Poly (*n*-BA-co-MMA) Binders." In *Preprints of the ICOM-CC 14th Triennial Meeting, The Hague,* ed. I. Verger, pp. 350–357. London: James and James.

Shank, W., and D. Norris. 2008. "Giving Contemporary Murals a Longer Life: The Challenges for Muralists and Conservators." In *Conservation and Access: Preprints of the IIC London Congress*, ed. D. Saunders, J. Townsend, and S. Woodcock, pp. 12–16. London: International Institute for Conservation. http://www.incca.org/component/content/article/126-diverse/427-selection-of-iic-articles (accessed 15 November 2010).

Smith, G. D. 2005. "A "Single-Shot" Separation and Identification Technique for Water Extractable Additives in Acrylic Emulsion Paints." In *Preprints of the ICOM-CC 14th Triennial Meeting, The Hague,* ed. I. Verger, pp. 824–832. London: James and James.

———. 2007. "Aging Characteristics of a Contemporary Acrylic Emulsion Used in Artists' Paints." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. Krueger, and M. Schilling, pp. 236–246. Los Angeles: The Getty Conservation Institute.

Snuparek, J. 1972. Some Factors Affecting the Water Absorption of Films from Synthetic Lattices. *Journal of the Oil and Colour Chemists Association*, 55:1007–1023.

Whitmore, P. M., and V. G. Colaluca. 1995. The Natural and Accelerated Aging of an Acrylic Artists' Medium. *Studies in Conservation*, 40:51–64. http://dx.doi.org/10.2307/1506611.

Whitmore, P. M., V. G. Colaluca, and E. Farell. 1996. A Note on the Origin of Turbidity in Films of an Artists' Acrylic Paint Medium. *Studies in Conservation*, 41:250–255. http://dx.doi.org/10.2307/1506544.

Zumbühl, S., F. Attanasio, N. Scherrer, W. Müller, N. Fenners, and W. Caseri. 2007. "Solvent Action on Dispersion Paint Systems and the Influence of Morphology—Changes and Destruction of the Latex Microstructure." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. Krueger, and M. Schilling, pp. 257–268. Los Angeles: The Getty Conservation Institute.

Surfactants and Acrylic Dispersion Paints: Evaluating Changes Induced by Wet Surface Cleaning Treatments

Bronwyn Ormsby, Elli Kampasakali, and Tom Learner

ABSTRACT. This paper summarizes recent research on the presence of surfactants on the surface of acrylic dispersion (emulsion) paint films and the impact of wet surface cleaning treatments on them. Empirical and analytical tests used to assess the presence of migrated surfactants to the film surface are described. The risks associated with conservation treatments are not always apparent at the time they are carried out. Findings from recent scientific research are therefore summarized into sections outlining current knowledge on the effects of surfactant removal through conservation treatment and aging and outlining the potential risks of the preservation of migrated surfactant on acrylic dispersion paint films. Surface surfactants are also discussed in the context of artists' intention, conservation ethics, cleaning efficacy, and the resoiling of cleaned paint films. Areas requiring further research have also been identified.

INTRODUCTION

Much of the significant body of recent research into the effects of surface cleaning treatments on acrylic dispersion (emulsion) paints is directed toward the role of non-volatile polyethoxylate (PEO)-based nonionic surfactant paint additives, which has been presented in detail elsewhere (Ormsby and Learner, 2009). These water-soluble materials are typically added as stabilizers and pigment-wetting agents at various stages of both the base dispersion and paint production (Croll, 2007). The amounts and types of surfactant present in bulk acrylic dispersion paint films vary with paint copolymer type, paint film age, pigment type, and brand (Ormsby et al., 2009). Despite the fact that these surfactants no longer serve their original function(s) after the paint film has dried, they remain distributed within the bulk film, continue to affect the paint's overall properties, and can migrate to the paint surface in significant amounts.

The precise mechanisms behind surfactant migration are still unclear; however, the process is somewhat dependent on surfactant concentration, paint film thickness, substrate type, and environmental conditions (Ormsby and Learner, 2009). The fact that these materials can be significantly impacted by surface cleaning treatments has prompted discussion on the significance of surfactants to the understanding, conservation, and preservation of acrylic dispersion works of art. This paper summarizes what is known and outlines some potential risks associated with the removal and/or preservation of migrated surfactants to the surface of acrylic dispersion paint films, aiming to encourage debate, clarify risk where possible, and support collection care decision-making processes.

Bronwyn Ormsby *and* ***Elli Kampasakali****, Conservation Department, Tate, Millbank, London SW1P 4RG, UK.* ***Tom Learner****, Modern and Contemporary Art Research, Getty Conservation Institute, 1200 Getty Center Drive, Suite 700, Los Angeles, California 90049, USA. Correspondence: Bronwyn Ormsby, bronwyn.ormsby@tate.org.uk; Elli Kampasakali, elinamoz@yahoo.com; Tom Learner, tlearner@getty.edu.* *Manuscript received 19 November 2010; accepted 24 August 2012.* *Contributions to this paper by T. Learner are Copyright © 2013 The J. Paul Getty Trust, all rights reserved.*

DISCUSSION

The Appearance of Migrated Surfactants

It is not easy to determine the presence of migrated surfactants on acrylic dispersion paint films through visual assessment alone. Surface surfactants are not going to be present on all films; however, where present, they can appear as matte spots or create a mottled surface effect, as shown in Figure 1, and may eventually form a coherent film, which may impart a hazy effect to the paint surface.

Combined soiling-surfactant layers can appear as light gray or white veils across paint surfaces, which can be visually distracting, particularly if additional marks and scuffs are also present. Recent case studies on surface cleaning treatments as part of the Tate AXA Art Modern Paints Project (TAAMPP) demonstrated that cleaned paint films often show a marked increase in color saturation, as shown in Figure 2, and that subtle surface textures were more visible (Ormsby, 2010).

The Presence of Migrated Surfactants

Tracking the progress of surfactant migration on several acrylic dispersion paint films with Fourier transform infrared–attenuated total reflectance spectroscopy (FTIR-ATR) has thus far indicated that naturally aged Talens paint films of the poly(ethyl acrylate/methyl methacrylate) (P(EA/MMA)) copolymer type (as per early acrylic paint formulations) tend to have high surfactant levels and that the group of three poly(*n*-butyl acrylate/methyl methacrylate) (P(*n*BA/MMA)) copolymer films tested tended to have lower levels, as shown in Figure 3 (Ormsby et al., 2009), suggesting that brand and base dispersion copolymer type play a significant role. However, recent investigations have indicated that some Liquitex P(*n*BA/MMA) paint samples are now beginning to register higher migrated surfactant levels (A. Soldano and B. Ormsby, Tate, unpublished internal report, "Cleaning Efficacy Study Report," 7 May 2010). Figure 3 also clearly illustrates that thermal aging (in this case at 60°C and 55% RH) accelerates post-ageing surfactant migration and that exposure to accelerated light aging (in this case with no UV component for equivalent to ~50 years of display) destroys the surface surfactant, presumably via photodegradation reactions (Ormsby et al., 2009).

It is not known how long it may take for surfactant layers to degrade through typical museum display conditions; indeed, surfactants have been detected on the surface of several works of art in Tate's collection dating from 1962 that have been infrequently displayed since acquisition (Ormsby et al., 2008b; Ormsby, 2010).

Identifying Migrated Surfactants

In addition to FTIR-ATR analysis, mass spectrometry techniques and mid-infrared reflectance spectroscopy have been used

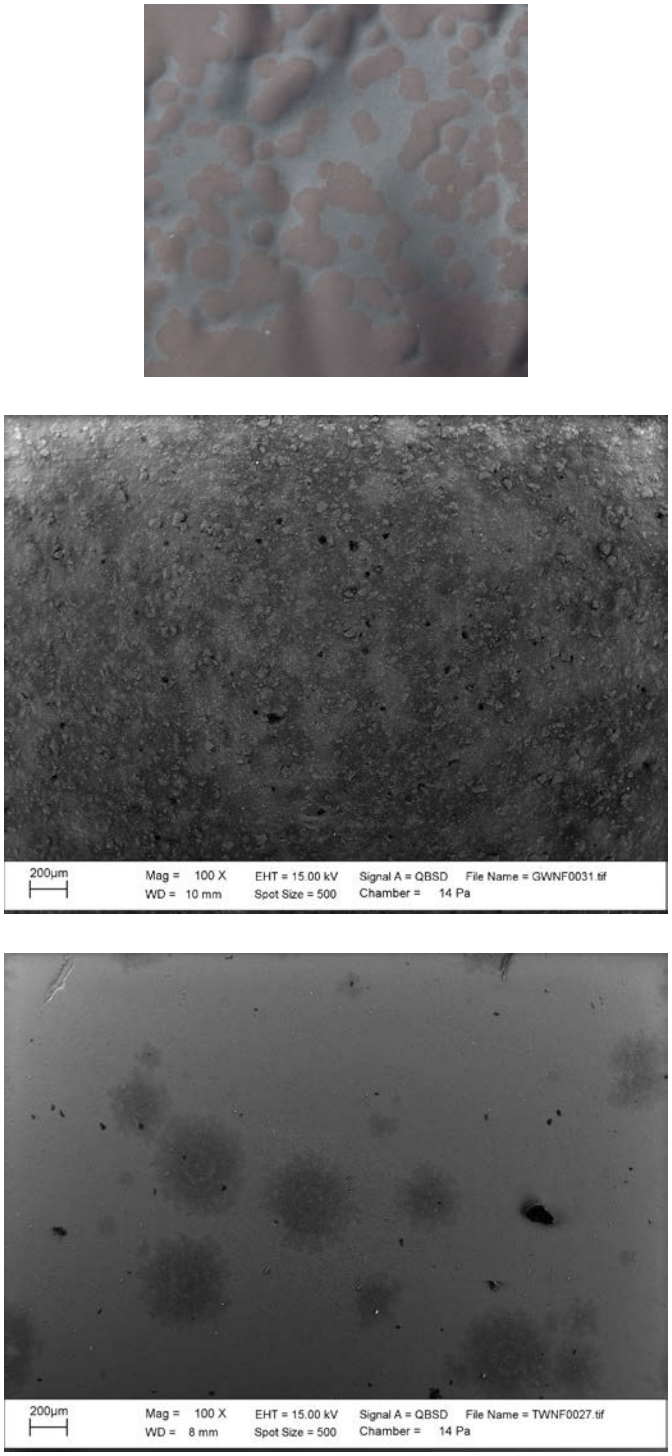


FIGURE 1. (top) Raking light photomicrograph of the mottled surfactant layer on a phthalocyanine green acrylic dispersion free film. Backscattered variable pressure SEM micrographs (100×) of surfactant migration on free films of titanium white from (middle) Winsor and Newton and (bottom) Golden Artist Colors. © Tate 2007, 2010.

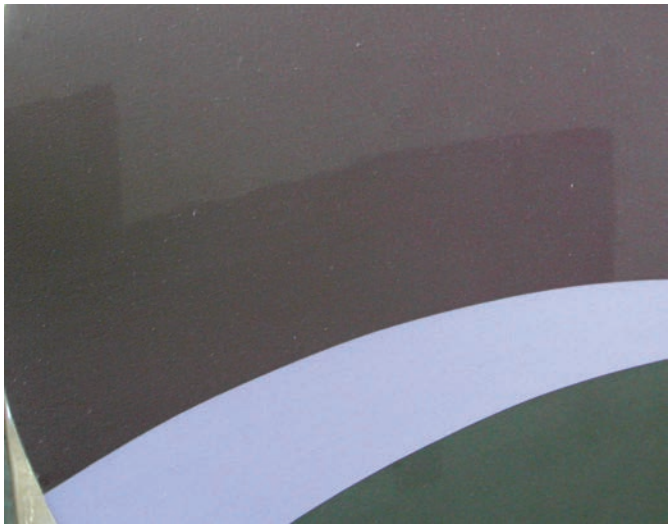


FIGURE 2. Raking light detail during treatment of Alexander Liberman's *Andromeda* (Tate accession number T00650). The dark area has been wet cleaned and illustrates the increased color saturation achieved though the removal of the combined soiling-surfactant layer. Tate 2007 © Alexander Liberman Trust.

to identify surfactants on painting surfaces and within aqueous extracts of bulk paint films (Ormsby et al., 2008b; Ormsby and Learner, 2009). A convenient, low-cost testing method for the identification of surfactants within a studio setting is not yet available and may become a research priority if surfactant materials become increasingly valued.

Aqueous paint surface extractions (assuming that paint films can take prolonged aqueous exposures) involving placing a droplet of deionized water (e.g., 60 μL) onto the paint surface for 1–2 minutes can, however, provide useful information. In the presence of significant quantities of surface surfactant, the diameter of the water droplet increases markedly when compared to films with no surfactant, as illustrated by the images included in Figure 4.

After observing the water droplet diameter, the extract can be drawn up and released onto a cavity slide and left to dry in dark, dust-free conditions. Once dry (or semidry), the extract can then be analyzed using transmission micro-FTIR spectroscopy (Ormsby et al., 2009). Although this is relatively rudimentary, PEO-based surfactants were identified on several case study paintings using this method (Ormsby et al., 2008b). The precise amount of migrated surfactant required for detection has not been established, but bubbles were often noted in extracts containing significant amounts of surfactant.

Surface conductivity tests also carried out on acrylic paint films (Ormsby, 2010; Soldano and Ormsby, 2010) have thus far not confirmed a direct relationship between surface conductivity and (nonionic) migrated surfactant abundance apart from a possible increase resulting from the larger water droplet diameters (increased surface area contact) facilitated by surfactant-rich paint surfaces.

Ethical Considerations and the Removal of Surfactants from Surfaces

The potential removal of surface surfactants during conservation treatment in the context of conservation ethics and artists' intention has been recently discussed (Learner and Ormsby, 2009).

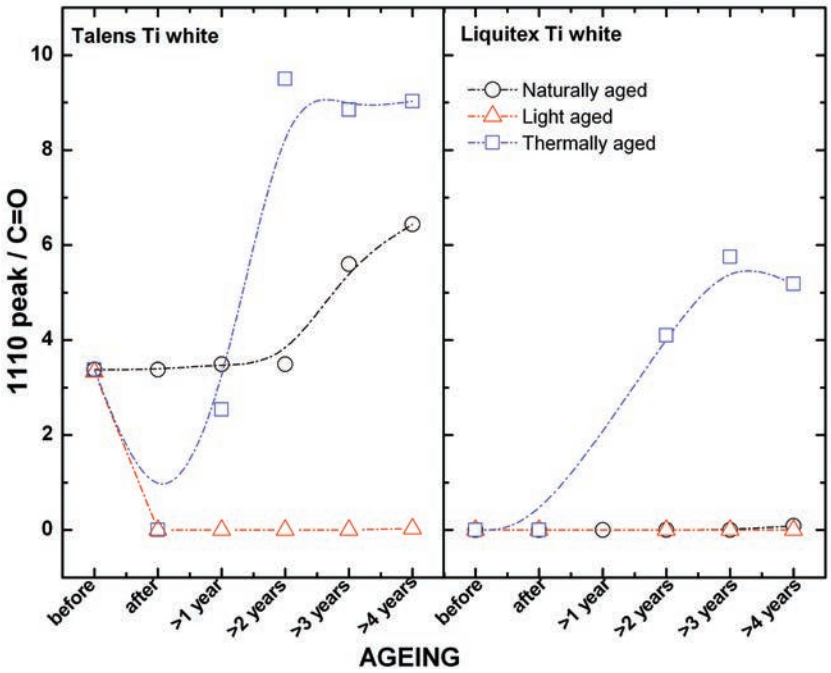


FIGURE 3. Tracking the presence of surfactant with FTIR-ATR analysis on titanium white paint films over four years. The *y* axis "before" figures reveal differences in initial surfactant levels; that is, the Talens sample (at 3.4) had more surfactant than the Liquitex sample (at 0.0).

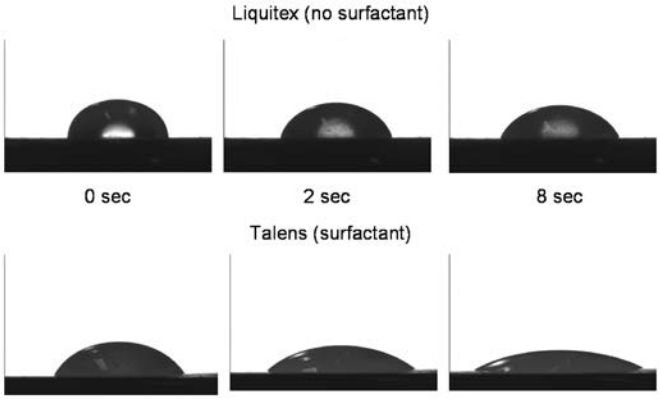


FIGURE 4. Photomacrographs of the behavior of water droplets on the surface of two titanium white acrylic dispersion paint free films: (top) Liquitex, with no surface surfactant, and (bottom) Talens, with high levels of surface surfactant. © Tate 2008.

The argument that these materials are original to these paints is, of course, valid; however, both the risks associated with preserving this layer and the practicalities of removing soiling without disturbing this layer are problematic and require further investigation.

Outside of conservation, paint manufacturers are aware of the surfactant migration process, and the house paint industry acknowledges that surfactants will be washed away (Golden Artist Colors, 2001:3–4). Within conservation, however, a recent study of paintings by Italian artists Alberto Burri and Sergio Lombardo described a presumed surfactant layer as a patina (De Cesare et al., 2009), and a recent interview with British artist Frank Bowling revealed his practice of adding soap flakes to the water he was using to dilute his acrylic paints to achieve a deliberate "graying out" or "veiled" effect on the paint surface (L. Mills and R. Barker, Tate, artist interview with Frank Bowling, 26 May 2009). Bowling stated that this was common practice amongst artists at that time (the early 1960s), which suggests that early acrylic dispersion paint surfaces may be more complicated still. In the light of these studies, it may prove beneficial to incorporate questions exploring these issues into artists' interviews.

Migrated Surfactants and Wet Cleaning Treatments

The PEO-based surfactants are highly vulnerable to removal with aqueous cleaning treatments. Thin surfactant layers can be removed with a few seconds of aqueous swabbing (Ormsby et al., 2009). Although nonpolar organic solvents do not directly dissolve these layers, surfactant can be partially removed or disturbed through mechanical action alone (Ormsby et al., 2008a), and blanching and pigment transfer have been noted with the use of these solvents (Golden Artist Colors, 2001:3–4). In addition, it is probable that dry-cleaning methods partially remove, disturb, or redistribute surfactant layers where present.

Changes in surface gloss after the aqueous wet-cleaning treatment of case study paintings were also detectable (see Table 1); however, it was impossible to distinguish the effect of the removal of surfactant from the simultaneous removal of the deposited soiling layer. It was also noted that where the combined soiling-surfactant layer was relatively thick, several passes of the swab were required for complete cleaning (Ormsby, 2010). Gloss readings taken from cleaned, unsoiled test paint films revealed that changes caused by the removal of migrated surfactant without soiling layers were of a similar range (Ormsby et. al., 2007).

Changes in bulk film mechanical properties arising from aqueous swabbing treatments have been found to be essentially indistinguishable from untreated control samples (Ormsby and Learner, 2009). However, any changes from light exposure and conservation treatment at the very surface of these paint films have yet to be fully explored.

After initial removal through one aqueous cleaning treatment, surfactant migration quickly resumes (Ormsby et al., 2009), and the rate of surfactant migration can be enhanced (post-cleaning) by increased temperatures (e.g. during travel). The surfactant is likely to continue migrating until either the reservoir within the paint film is exhausted or the driving forces behind the migration process (which may include the removal of surfactant layers through cleaning or exposure to light) are minimized.

TABLE 1. Gloss changes (measured at a 60° angle) induced by wet surface cleaning treatments for five of the acrylic dispersion paintings cleaned as part of the Tate AXA Art Modern Paints Project (TAAMPP).

Artist	Painting title (Accession number)	Date	Range of change in gloss units (all colors) after treatment
Jeremy Moon	*Untitled 2/72* (T02052)	1972	–0.4 to 2.0
Jeremy Moon	*Hoop-la* (T012240)	1965	+0.1 to 1.0
Alexander Liberman	*Andromeda* (T00650)	1962	–0.2 to 0.8
John Hoyland	*25.4.69* (T01129)	1969	–1.7 to +1.3
Bernard Cohen	*Painting with Three Spots, Two Yellow and One Blue* (T01538)	1970	+0.1 to 2.3

General Concerns with Wet-Cleaning Treatments

Although beyond the scope of this paper, other issues associated with applying wet surface cleaning treatments to acrylic dispersion paint films are naturally of high importance. These include: the abrasion and burnishing of paint surfaces, pigment loss, paint swelling, cleaning system residues, and the extraction of soluble paint components. Several of these aspects have been addressed elsewhere (Ormbey and Learner, 2009).

Surfactant, Soiling Removal Efficacy, and the Resoiling of Cleaned Films

The TAAMPP case study treatments (Ormsby, 2010) and recent soiling removal studies have confirmed that deposited soiling (and surfactant) is generally more efficiently removed from acrylic paint surfaces using aqueous wet-cleaning systems (Ormsby et al., 2007; Soldano and Ormsby, 2010). As stated earlier, nonpolar organic solvents remove less surfactant; however, they are also markedly less efficient at removing soiling.

During recent studies, the presence of a substantial surfactant layer was noted as possibly enhancing the removal of soiling from heavily soiled paint films. It may be the case that the surfactant acts as an additional cleaning agent or as a release layer. However, it is possible that a substantial surfactant layer may also act as a physical barrier to the permanent embedding of soiling, which has potential repercussions for the resoiling of surfactant-free films. An ongoing study at Tate into the passive soiling of a series of treated and untreated paint films (with and without surface surfactant) will hopefully contribute to our understanding of these issues in the near future.

Potential Effects of the Preservation of Surfactants on the Surface

When contemplating the decision to preserve a migrated surfactant layer on an acrylic dispersion paint film, artists' intention, appearance, and the empirical and scientific information available on possible repercussions for future condition need to be considered. It is probable that hygroscopic surfactant layers retain deposited soiling, and the potential action of radical species created during the photodegradation of PEO surfactants requires investigation; however, little evidence exists for paint degradation caused by the presence of migrated surfactant layers.

Nonetheless, the permanent embedding of deposited soiling into paint films can be a risk when soiling is not removed. The embedding process is not necessarily dependent on the presence or absence of a surfactant layer; however, choosing not to clean a work of art inherently increases the risk of embedded soiling. This clearly requires further investigation, with the aim of determining optimal cleaning cycle frequency.

Water has been found to play a role in the embedding process, which also highlights one of the inherent risks of wet-cleaning these paint films. Deionized water droplets applied to soiled acrylic dispersion paint films caused the permanent embedding of soiling when allowed to dry naturally, as demonstrated in Figure 5. This suggests that soiling should be routinely removed from these paint films and, equally, that the use of water (and other solvents) should be carefully controlled. Recent studies have, however, also revealed that soiling can be embedded without any contact with water (Soldano and Ormsby, 2010). It is therefore also important to determine whether migrated surfactant layers contribute to the embedding process or whether they act as a physical barrier to the embedding of soiling.

CONCLUSIONS

This paper attempts to contextualize information relating to migrated surfactant layers on the surfaces of acrylic dispersion-based paint films. Although research in this area is ongoing, summarizing current knowledge on the pros and cons of the removal or preservation of these layers is beneficial.

Concerns about surfactant removal during treatment need to be considered within the context that surfactants may not always be present, can be present on specific paint passages only, can be degraded by light, and will be at least partially removed, reduced, or redistributed by most cleaning and varnishing processes and that the ability to remove deposited soiling without also affecting the surfactant layer (if present) is essentially impossible. In addition, it has been found that surfactants continue to migrate after one aqueous treatment; hence, removal does not necessarily ensure a surfactant-free paint surface in the future.

The decision to remove, reduce, or preserve surfactant layers also needs to be considered with respect to ethical and aesthetic requirements, as migrated surfactant originates from within acrylic dispersion paint films and can therefore be described as a patina. In some cases this layer may be of aesthetic and historical importance to individual artists or groups of works.

The decision to preserve surfactant layers also requires an evaluation of the potential aesthetic consequences, including a gradual loss of color saturation and the masking of surface texture as the layer increases in thickness and attracts soiling. The partial removal of soiling-surfactant films as a compromise option can also be difficult to achieve, often resulting in uneven gloss and color saturation.

The greatest risk associated with not removing deposited soiling, however, is the permanent embedding of soiling into these paint films. In this case, none of the currently available wet- and dry-cleaning systems, including newly introduced options (Ormsby and Phenix, 2009), will be particularly effective.

Despite the growing body of scientific research characterizing the properties of these paints, assessing the risks associated with migrated surfactant removal or preservation remains somewhat hampered by a lack of information. Perhaps even more pressing for practicing conservators faced with works of art of unknown paint types is the need to find an easy-to-use, reliable, low-cost method for determining whether a work of art contains

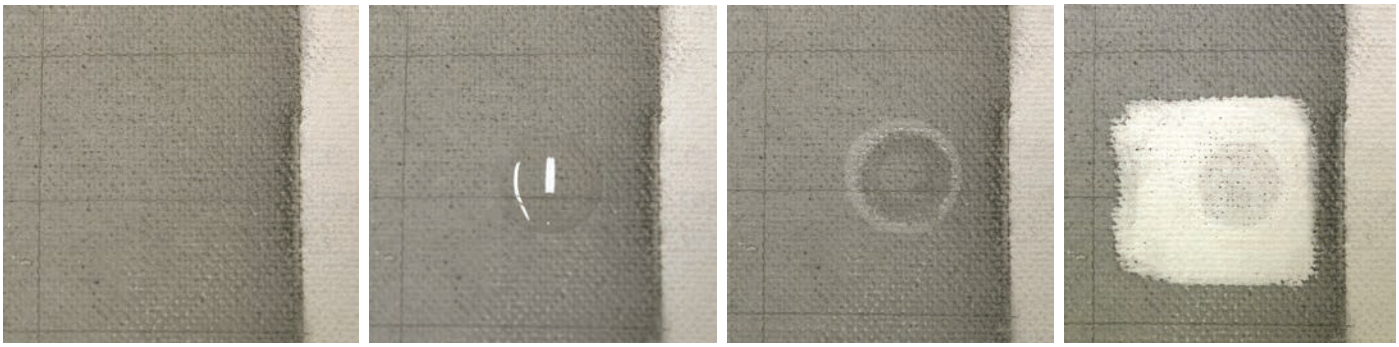


FIGURE 5. From left to right, detail of a soiled Talens titanium white paint film, deionized water droplet placed onto the soiling layer, dried water droplet two days later, and the same section after swabbing with water, demonstrating that the water droplet helped embed the soiling into the paint film, making it harder to clean. © Tate 2010.

acrylic dispersion paints and whether migrated surfactant is actually present.

Acknowledgments

The authors thank Alexia Soldano, Patricia Smithen, Rachel Barker, Laura Mills, and Lise Chantrier Aasen of Tate, London; Simone Musso, formerly of Politecnico di Torino, Turin, Italy; Grazia de Cesare of the Istituto Centrale per il Restauro; Alex Ball of the Natural History Museum, London; and AXA Art Insurance (http://www.axa-art.co.uk) for funding the TAAMPP research at Tate from 2006 to 2009.

REFERENCES

Croll, S. 2007. "Overview of Developments in the Paint Industry since 1930." In *Modern Paints Uncovered: Proceedings of the Modern Paints Uncovered Symposium,* ed. T. Learner, P. Smithen, J. W. Krueger, and M. R. Schilling, pp. 17–29. Los Angeles: The Getty Conservation Institute.

De Cesare, G., P. Iazurlo, F. Capanna, and M. Coladonato. 2009. "The 'Patina' of the Acrylic-Vinyl Emulsion Paintings." In *Art Today, Cultural Properties of Tomorrow. The Conservation and Restoration of Contemporary Artwork. Proceedings of the SF-IIC Conference,* ed. M. Stefanaggi and R. Hocquette, p. 343. Paris: Institut National du Patrimoine.

Golden Artist Colors. 2001. Conservation of Acrylic Paintings. *Just Paint*, 9:1–10.

Learner, T., and B. Ormsby. 2009. "Cleaning Acrylic Emulsion Paints: Putting Research into Context." In *Art Today, Cultural Properties of Tomorrow. The Conservation and Restoration of Contemporary Artwork. Proceedings of the SF-IIC Conference,* ed. M. Stefanaggi and R. Hocquette, pp. 193–199. Paris: Institut National du Patrimoine.

Ormsby, B. 2010. Tate AXA Art Modern Paints Project (TAAMPP): 2006–2009 Research Summary. http://www.tate.org.uk/download/file/fid/4480 (accessed 13 November 2012).

Ormsby, B., E. Hagan, P. Smithen, and T. Learner. 2008a. "Comparing Contemporary Titanium White-Based Acrylic Emulsion Grounds and Paints: Characterization, Properties and Conservation." In *Preparation for Painting: The Artists' Choice and Its Consequences*, ed. J. H. Townsend, T. Doherty, G. Heydenreich, and J. Ridge, pp. 163–171. London: Archetype.

Ormsby, B., E. Kampasakali, C. Miliani, and T. Learner. 2009. An FTIR-Based Exploration of the Effects of Wet Cleaning Artists' Acrylic Emulsion Paints. *e-Preservation Science,* 6:186–195.

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.

Ormsby, B., T. Learner, G. Foster, J. Druzik, and M. Schilling. 2007. "Wet-Cleaning Acrylic Emulsion Paint Films: An Evaluation of Physical, Chemical and Optical Changes." In *Modern Paints Uncovered: Proceedings of the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. W. Krueger, and M. R. Schilling, pp. 187–198. Los Angeles: The Getty Conservation Institute.

Ormsby, B., and A. Phenix. 2009. Cleaning Acrylic Emulsion Paintings. *Conservation Perspectives: The GCI Newsletter,* 24:2. http://www.getty.edu/conservation/publications/newsletters/24_2/cleaning.html (accessed 13 November 2012).

Ormsby, B., P. Smithen, F. Hoogland, T. Learner, and C. T. Miliani. 2008b. "A Scientific Investigation into the Surface Cleaning of Acrylic Emulsion Paintings." In *Preprints ICOM-CC 15th Triennial Conference, New Delhi,* ed. J. Bridgland, Volume 2, pp. 857–865. New Dehli: Allied Publishers.

Extended Abstract—Effects of Solvents on the Physical Properties of Polymeric Films

Mareike Opeña and Elisabeth Jägers

INTRODUCTION

Solvents are used for many purposes in the conservation field. The conservation professional standard recommends using solvents of the highest purity to enable reaction predictability and avoid possible harmful residues (Lorenz, 1998). Solubility parameters explain why solutions show different qualities, depending on the affinity between solvent and polymer (Feller et al., 1985). It is assumed that each solvent leaves the polymer in a certain molecular arrangement, with more or less inner equilibrium, leading to different mechanical properties that may reflect physical aging reactions (Hansen et al., 1991). In a "good solution" the molecules are fully unfolded, and each functional group along the polymer chain is occupied by the corresponding functional group of a solvent. In a "poor solution" some parts of the polymer molecule remain entangled. These molecular arrangements persist through the drying process, even exceeding the no-flow point. They become an immanent part of the film (Hansen et al., 1991).

A dried film from a good solution appears smooth, with an even molecular chain interaction of the many different molecules, whereas a poor film appears inconsistent and porous, with a rough (matte) surface (McGlinchey, 1993; Menck-Schaa et al., 2008). In particular, the evaporation time of a solvent seems to influence the quality of the formed film (Feller et al., 1985). The faster a solvent leaves the freshly applied wet film, the sooner the molecules will lose their chain mobility (Marrion, 1994). They are thus hindered from building an inner equilibrium of charges and free volume (Schilling, 1988), which leaves a fragile film prone to physical aging reactions (Brydson, 1999).

To assess the effect of solvents on the film-building quality of polymers, a thermal analysis study was undertaken. The aim of this paper is to foster research in this very important and underestimated aspect of solvent use in conservation.

MATERIALS AND METHODS

Four materials, Paraloid B72, Laropal A81, MS2A, and Regalrez 1094, were chosen, and each was dissolved in six to seven solutions at 20% by weight in various solvents (Table 1). The films were applied to smooth glass surfaces with a film thickness of 60 μm. After eight months of drying, the samples were analyzed by thermal analysis. Since the only

***Mareike Opeña**, Contemporary Conservation Ltd., 460 West 4th Street, 3rd Floor, New York, New York 10001, USA. **Elisabeth Jägers**, Cologne Institute for Conservation Sciences, Ubierring 40, 50678 Cologne, Germany. Correspondence: Mareike Opeña, mareike.opena@gmail.com; Elisabeth Jägers, e-e.jaegers@t-online.de.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

differing parameter in the samples is the solvent used, any variation in the results could be attributed to the solvent's influence.

Thermal gravimetrical analysis (TGA) measures mass changes of samples as a function of time and temperature (Kittel, 2006). Each sample was measured once with the same heating program (heat rate of 10°C/min), allowing us to measure the solvent retention within the sample.

Differential scanning calorimetry (DSC) reveals thermal changes. Following ASTM International (1998) standards, samples were exposed to two heating periods (heat rates of 10°C/min, cooling of 10°C/min). The first period reflects the influence of physical aging reactions, whereas the second one is free from any thermal history and reveals the subtler influences of the molecular arrangement (Table 1).

RESULTS AND CONCLUSIONS

Solvent Retention

The overall solvent retention was much higher than expected, which is surprising, taking into account the age of the samples. Three different reasons for solvent retention were found: (1) slow evaporation rate, (2) very good solvent-polymer interaction, regardless of high evaporation rate, and (3) in the case of solvent mixtures, one solvent acting as an intermediary between the polymer and the poor solvent, causing retention of both solvents.

Glass Transition Temperature

The measured glass transition temperature T_g for all samples was far below that reported in the literature. This may be because DSC usually reports lower T_g than other methods (e.g., differential thermal analysis [DTA]; A. Phenix, Getty Conservation Institute, personal communication). Within one material, however, the films showed massive deviations of T_g of up to 20°C. The reasons for these differences were interpreted as follows:

- Solvent retention decreases T_g.
- The physical properties of these films are strongly influenced by those at interfaces, which can differ strongly from those of the bulk material (García-Turiel and Jérome, 2007).
- Slow solvent evaporation causes extended chain mobility, and the adjustment of these results in a denser equilibrium film and, consequently, in a higher T_g.

TABLE 1. List of solutions, T_g measurements (DSC), and solvent retention (TGA) after eight months of drying. MS2A revealed strong chemical reactions in both DSC and TGA between 70°C and 120°C. It is assumed that the evaporation of chemical reaction products causes the massive weight loss and elevated T_g. DSC = differential scanning calorimetry, TGA = thermal gravimetrical analysis, NT = not treated, 0 = no residues found, T_g = glass transition temperature for the second heating period with DSC, SR = solvent retention, SGB (Siedegrenzbenzin) = aliphatics, traces of aromatics, and boiling range according to the number (e.g., SGB 60–95 indicates boiling point between 60°C and 95°C), Shellsol A = 100% pure aromatics, Shellsol D40 = 40% naphthenes, <5% aromatics, Shellsol T = aliphatics, no aromatics.

Paraloid B72			Laropal A81			MS2A			Regalrez 1094		
Solvent	T_g (°C)	SR (%)	Solvent	T_g (°C)	SR (%)	Solvent	T_g (°C)	SR (%)	Solvent	T_g (°C)	SR (%)
Acetone	36.8	0	Isooctane, Shellsol A (6:4)	26.2	NT	Isooctane	66.3	7	Isooctane	24.4	0
Toluene	38.6	0	SGB 60–95, Shellsol A (6:4)	33.2	0	SGB 60–96	61.8	7	SGB 60–95	NT	NT
Xylene	36.2	0.5	SGB 100–140, Shellsol A (6:4)	30.5	1	SGB 100–140	62.3	7	SGB 100–140	NT	NT
Shellsol A	28.4	1	Shellsol D40, Shellsol A (6:4)	30.3	0.75	Shellsol D40	64.7	7	Shellsol D40	23.7	0
Ethanol	NT	NT	Acetone	46.2	0	Shellsol D40, isopropanol (2:8)	65.1	7	Shellsol D40, isopropanol (2:8)	24.9	0
Acetone, toluene, Shellsol A (45:45:10)	28.4	1	Methyl ethyl ketone	45.1	0	Shellsol A	63.2	7	Shellsol A	24.7	0
			Isopropanol	46.1	0	Isooctane, SGB 100–140, Shellsol T (45:45:10)	64.7	7	SGB 60–95, SGB 100–140, Shellsol D40 (45:45:10)	20.9	0

- The solvent's influence on the molecular arrangement is so high that it cannot be eliminated by heating above T_g, as they are still apparent in the second heating period of the DSC program.
- All components in a mixture appear to influence the inner equilibrium and molecular arrangement of a film.

The size and shape of a solvent's molecules, its polarity, and its evaporation rate, among other properties, influence the molecular arrangement within a film. The solution quality and drying rate lead to different inner configurations of the molecules within a film. This explains the different mechanical properties observed and may explain the faster-appearing physical aging reactions in some films. Solvent retention seems to interfere strongly and hinders the development of thermal history. Good solutions lead to more elastic, ductile films, whereas poor solutions form brittle, but stronger, films with higher inner tension.

This hypothesis is important for a variety of conservation aspects since the material's appearance, brittleness or elasticity, adhesive and cohesive strengths, and durability are most likely influenced by the choice of solvent. Understanding the dependencies of the polymer's behavior based on the previously used solvent(s) could establish a more appropriate selection of both components for conservation purposes. For this purpose, the following aspects need to be further researched: (1) the solvent's influence on material mechanical properties, e.g., flexibility, (2) time frame of the deterioration processes by comparing films of different ages, (3) the solvent's influence on the molecular arrangement of the paint layers' binding media during cleaning processes or when applying a varnish, (4) an analysis of the predictability of solvent mixtures, and (5) a comparison of the solvent's intrinsic volatility and evaporation rates from solutions.

Acknowledgments

The authors thank Michael Groteklaes, Coatings Department at the Institute of Chemistry, Hochschule Niederrhein Krefeld, Germany, for his kind support by providing TGA and DSC analysis for all sample measurements.

REFERENCES

ASTM International. 1998. Standard Test Method for Tensile Properties of Organic Coatings. Standard ASTM D 2370-98. West Conshohocken, Pa.: ASTM International.

Brydson, J. A. 1999. *Plastics Materials*. 7th ed. Oxford: Butterworth-Heinemann.

Feller, R. L., N. Stolow, and E. H. Jones. 1985. *On Picture Varnishes and Their Solvents*. Washington, D.C.: National Gallery of Art.

García-Turiel, J., and B. Jérome. 2007. Solvent Retention in Thin Polymer Films Studied by Gas Chromatography. *Colloid Polymer Sciences,* 285:1617–1623. http://dx.doi.org/10.1007/s00396-007-1733-6.

Hansen, E. F., M. R. Derrick, M. R. Schilling, and R. Garcia. 1991. The Effects of Solution Application on Some Mechanical and Physical Properties of Thermoplastic Amorphous Polymers Used in Conservation: Poly(vinyl acetate)s. *Journal of the American Institute for Conservation,* 30(2):203–213. http://dx.doi.org/10.2307/3179532.

Kittel, H. 2006. *Lehrbuch der Lacke und Beschichtungen: Analysen und Prüfungen*. [Textbook on Laques and Coatings: Analysis and Testing.] Volume 10. 2nd ed. Stuttgart, Germany: Colomb Verlag.

Lorenz, G. 1998. *Mit Lösungsmitteln Rechnen*. [Reckoning with Solvents.]. Hamburg, Germany: G. Lorenz.

Marrion, A. 1994. *The Chemistry and Physics of Coatings*. Cambridge: Royal Society of Chemistry.

McGlinchey. C. 1993. "The Physical Aging of Polymeric Materials." In *Saving the Twentieth Century: The Degradation and Conservation of Modern Materials*, *Symposium '91,* ed. D. W. Grattan, pp. 113–122. Ottawa: Canadian Conservation Institute.

Menck-Schaa, A., K. Schulte, and L. Reuber. 2008. *Firnis: von matt bis glänzend*. [Varnishes: From Matte to Brilliant.] Edited by H. Portseffen. Kölner Beiträge zur Restaurierung und Konservierung von Kunst und Kulturgut 19. Munich, Germany: Siegl Fachbuch Handlung.

Schilling, M. R. 1988. The Glass Transition of Materials Used in Conservation. *Studies in Conservation,* 34:110–116.

Extended Abstract—The Removal of Commercial Varnishes from Acrylic Paints

Marie-Catherine Cyr, Emily Min, and Alison Murray

INTRODUCTION

In her article from the "Modern Paints Uncovered" conference, Smithen (2007:166–167) states "Some currently available commercial varnishes are formulated to be removed, but there are no reports in the conservation literature discussing successful removal of these coatings from acrylic paintings." The present research attempts to address this by investigating different commercially available varnishes (Cyr, 2007; Min, 2009). Although varnishes are commonly applied to many traditional oil paintings, the same is not true for modern and contemporary works. Acrylic paint manufacturers and some artists have suggested that acrylics require an additional protective coating; however, removing such a coating with solvents could harm the underlying acrylic, possibly partially dissolving it and leaching additives (Quillen Lomax and Fisher, 1990; Samet, 1998; Jablonski et al., 2003; Learner, 2004). The effect of wet-surface cleaning on acrylics using aqueous solution and solvent systems has been studied by a number of researchers, including Ormsby and Learner (2009), whose review article gives an overview of this topic. The research presented here describes the level of difficulty when removing the varnish layer from acrylic paint samples and documents resulting changes to the paint layer.

EXPERIMENT

Two studies were performed following manufacturers' directions for varnish removal. The first study used Soluvar Gloss Picture Varnish (Soluvar), an *n*-butyl and isobutyl methacrylate, to coat acrylic paint samples from Liquitex Artist Materials and Mineral Spirit Acrylic Gloss Varnish (MSA), a solution of isobutyl and *n*-butyl methacrylate (Golden Artist Colors, 2006), to coat acrylic paint samples from Golden Artist Colors. Ultramarine blue and titanium white paint samples were first left to dry for different periods: one week, two months, and eight years. The eight-year-old paint samples had been cast on Mylar (4 mils thick) for a previous study; therefore, the new samples were prepared following the same method. Paint strips (0.2 mm thick and 5 cm wide) were first cast onto Mylar and left to naturally age for the desired length of time. Strips (2.5 × 7.5 cm) were then cut from all samples and applied to glass slides. The coatings were prepared as indicated by the manufacturer, brushed in a single stroke onto the samples, left on for one week or one month, and then removed by lightly rolling cotton

***Marie-Catherine Cyr**, Paintings and Contemporary Art, National Gallery of Canada, 380 Sussex Drive, Ottawa, Ontario K1N 9N4, Canada. **Emily Min**, Fraser / Spafford Ricci Art & Archival Conservation Inc., 2276 134th Street, South Surrey, British Columbia V4A 9T9, Canada. **Alison Murray**, Art Conservation Program, Department of Art, Queen's University, 15 Bader Lane, Kingston, Ontario K7L 3N6, Canada. Correspondence: Marie-Catherine Cyr, mcyr@gallery.ca; Emily Min, emily@fsrconservation.com; Alison Murray, alison.murray@queensu.ca.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

swabs dipped in different organic solvents. The number of passes with the swab for the coating to be completely removed varied from one sample to the next. The manufacturer-recommended solvents were first used, and when they were found to be ineffective, more polar solvents were tested. This procedure was used to emulate a real-life studio scenario where a variety of solvent mixtures would be tested. Free films of varnish on glass slides were also made and naturally aged in ambient conditions for one week or one month. Several techniques were used to record the condition of the surfaces before coating with the varnish and after its removal, including color and gloss measurements and scanning electron microscopy (SEM) of select samples. The free films were also examined using Fourier transform infrared (FTIR) spectroscopy, as well as color and gloss analysis. Differential scanning calorimetry was used to determine if the solvent had any effect on the glass transition temperature T_g of the acrylics.

The above-mentioned samples did not include isolation barriers since it was felt that some artists would not follow the manufacturers' recommendations. Therefore, additional samples were prepared with isolation barriers as recommended by the two manufacturers (Liquitex Gloss Varnish for the Liquitex samples and Golden Soft Gel Gloss diluted 2:1 with water for the Golden samples) before varnishing. These samples were only observed visually to detect changes in color, gloss, and surface texture, and the handling properties were noted.

The second study used Golden Polymer Varnish, an acrylic-styrene copolymer solution containing ammonia and propylene glycol, with ultraviolet light stabilizers (UVLS), i.e., benzotriazolyl-OH-butylphenyl propionate, in both gloss and matte versions; this waterborne coating is meant to be removable by alkaline reagents. Research has found that acrylic emulsion paint has a tendency to swell when using water and aqueous solutions within a specific pH range for wet-cleaning treatments; acrylic paints may slightly swell at a pH of 4 or 5 and below, and they swell significantly when exposed to a pH above 8 (Ormsby and Learner, 2009). The purpose of this study was to examine the removability of this widely available waterborne coating and the effect on acrylic emulsion paint films when removed using alkaline reagents, specifically following instructions recommended by the manufacturer. The samples were prepared on the basis of common materials and techniques available to artists in the preparation and execution of acrylic paintings. Acrylic emulsion paint samples were cast onto untempered Masonite panel supports prepared with Golden Acrylic Gesso, 2.5 × 7.5 cm in dimension, with a consistent thickness of 0.2 cm. Each panel had 15 acrylic paint films: 5 titanium white films, 5 ultramarine blue films, and 5 cadmium red medium films (Figure 1).

The acrylic paint samples were left to dry for either one week or 50 days before being brush varnished. The coatings were either naturally aged for one week or one month or were placed under UVA fluorescent light (long-wave UV) in a Q-Lab QUV test chamber for 1200 hours to represent 100 years of indoor UV light exposure. Free films of varnish were exposed to the same conditions. Three alkaline reagents, suggested by the manufacturer, were used to remove the varnish, Goldex household ammonia, *N*,*N*-dimethylethanolamine (DMEA), and AMP-95 (2-amino-2-methyl-1-propanol), and two different concentrations were tested for each of these reagents. Cotton swabs were dipped in the reagent and rolled over the test samples in a uniform and consistent manner, applying little to no force on the swab. Depending on the activity of the reagent, rolling was carried out for a few seconds to one minute, until the varnish was completely removed from the paint samples. The speed and ease of the solubilization and removability of the coatings were rated according to each solution as being insoluble, partially soluble gel, soluble, or readily soluble. The SEM of selected samples, FTIR spectroscopy, and testing for solubility, color, and gloss evaluations were carried out. As the two main studies were performed in different years, no direct comparison for the amount of pigment pickup during varnish removal could be made.

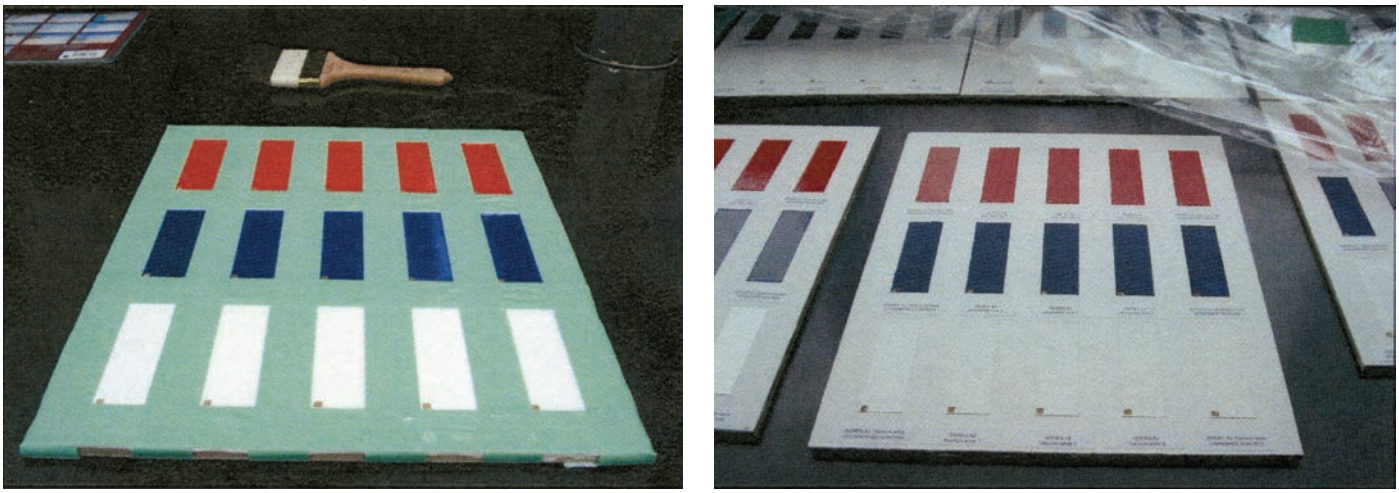


FIGURE 1. Cast acrylic emulsion paint samples with the painter's tape borders (left) built up to a depth of 0.2 cm and (right) removed.

RESULTS AND DISCUSSION

For the first study, solubility evaluation showed that only mineral spirits were required to remove the MSA varnish from the Golden paint samples; however, for removal of Soluvar from the Liquitex paint samples, a 1:1 mixture of xylene or ethanol with mineral spirits was needed to resolubilize the coating (the first mixture had less visual impact on the paint films). No pigment release was noted after a single pass with mineral spirits on the uncoated, cured samples, although upon a second pass on the Liquitex samples and a third pass on the Golden samples, the swab started to visibly pick up some color. The samples were sensitive to all other solvents tested. There were minimal differences between the free films cured for one week and one month in terms of gloss, solubility, and FTIR spectra, and there was a slight tendency for yellowing.

The measured color change for titanium white after varnish removal was not significant. Some variation in color apparent in ultramarine blue, the darker and more sensitive color, was linked to the age of the acrylic paint films rather than the length of time the varnish was left on the paint film, although the results were not consistent for whether an older film or a younger film caused the least change for different manufacturers. Liquitex showed the smallest change in color for the ultramarine blue for paint samples cured for eight years, whereas Golden showed the smallest change in ultramarine blue for samples cured for one week. More work is needed to explain these results. Greater general variations in gloss after varnish removal were observed for Liquitex samples in the white and Golden samples in the ultramarine. The one-week-old and eight-year-old paint samples varnished for one week were analyzed with SEM before and after the varnish was removed; no samples showed any notable topographical change. The differential scanning calorimetry results showed no significant change in T_g.

In the additional samples prepared according to the manufacturers' specifications, the intermediate layer was meant to remain on the paint layer permanently to protect it from being adversely affected by any varnishing or varnish removal process. As noted through visual examination, the presence of the isolation layer was found to alter the color, gloss, and texture of the paint layer significantly for both sets of samples. A marked darkening of the ultramarine blue films occurred in both the Liquitex and Golden samples upon application of the isolation layer. Once saturated by this coating, the color did not noticeably vary again upon varnishing or varnish removal. In addition, the presence of the isolation layer considerably increased the gloss of all samples and also altered their surface texture. Although the manufacturers' instructions were followed diligently, the handling properties of both isolation layers were found to impact the results greatly. The Liquitex Gloss Varnish used as the isolation layer for the Liquitex samples dried too quickly and was not self-leveling; therefore, brushstrokes remained visible, affecting the surface texture and ultimately the gloss as well. Although the Soluvar applied over this layer had very good working properties, once it was removed, which required extensive swabbing, the unvarnished surface had an uneven gloss as some varnish was still lodged in the textured isolation layer. The Golden Soft Gel Gloss solution used as the isolation layer for the Golden samples had better working properties, but it was still very difficult to get a brushstroke-free application. The gloss increased and the surface texture was altered, but varnishing with MSA leveled the surface. As previously discussed, varnish removal in this case proved easier than with the Liquitex samples and seemed to take away a very thin film from the isolation coat, slightly evening out its texture. The resulting surface was quite smooth and less glossy than with the varnish.

For the second study, only minor changes in gloss were detected for the free films. There was no significant color change for the naturally aged samples, and these samples could be solubilized in the alkaline reagents. For the UVA-exposed samples, the matte films became slightly darker, and both the matte and the gloss films became slightly more yellow. Solubilizing these samples required more time and a higher concentration of alkaline reagent (Table 1). The FTIR spectra did show differences in the matte varnish after aging, possibly indicating chemical changes due to the presence of amorphous silica used as the matting agent; these samples were also more soluble compared to the gloss samples (Figure 2).

TABLE 1. Solubility testing of the different aged free varnish films using Goldex household ammonia, DMEA, and AMP-95. I = insoluble, PS = partially soluble, S = soluble, RS = readily soluble.

		Varnish naturally aged 7 days		Varnish naturally aged 30 days		Varnish exposed to UVA light for 1200 hours	
Alkaline reagent	**pH**	**Gloss**	**Matte**	**Gloss**	**Matte**	**Gloss**	**Matte**
Goldex, full concentration	10.5	RS	RS	RS	RS	S	S
Goldex and distilled water, 1:1	10.5	S	S	S	S	PS	PS
DMEA, full concentration	11	RS	RS	RS	RS	S	S
DMEA and distilled water, 1:1	11	S	S	S	S	S to PS	S to PS
AMP-95, full concentration	11	PS	PS	PS	PS	PS to I	PS to I
AMP-95 and 10% distilled water	11	PS	PS	PS	PS	PS to I	PS to I

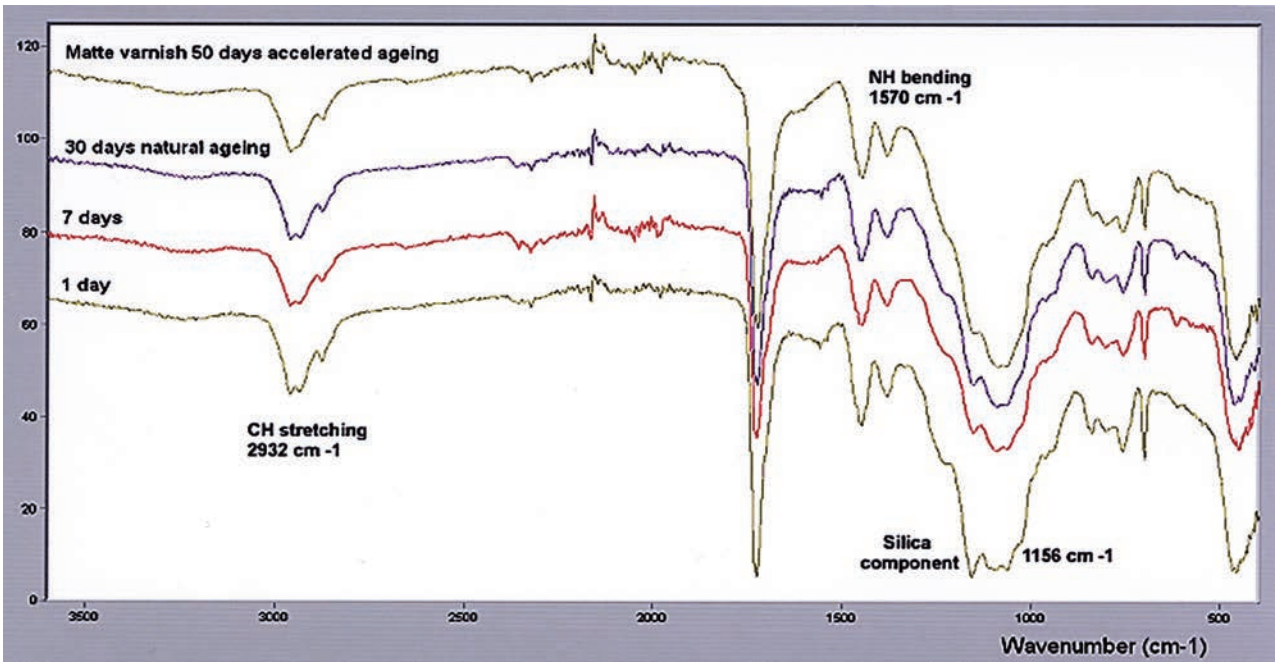


FIGURE 2. Infrared absorption spectra of polymer varnish with UVLS, matte, after 1, 7, and 30 days of natural aging and 1200 hour exposure to UVA light.

After one month of natural aging, the varnish required slightly stronger alkaline solutions for effective removal, at a pH range of 11–12. The UVA-aged samples were the least soluble, requiring a higher concentration as well as more mechanical action and repeated clearance with distilled water, thus potentially incurring the greatest physical change. Because of overall handling properties, Goldex household ammonia proved to be the most effective reagent. The DMEA solubilized the varnish as readily and in less time; however, the swab turned a bright yellow color when picking up the solubilized varnish, which was not the case with either Goldex or AMP. The AMP was the least successful reagent; it required considerably more time to solubilize and remove the varnish and, being slightly viscous, made clearance more difficult and required repeated applications of distilled water. All alkaline reagents had difficulty in removing the milky white solubilized Polymer Varnish, and repeated swabbing with distilled water was needed for it to be fully cleared and rinsed off the surface. Pigment transfer from the acrylic emulsion paint samples onto cotton swabs was observed with all the alkaline solutions tested to remove the coatings. Once the coating was solubilized with repeated swabbing and the barrier between the varnish and acrylic emulsion paint film surface was broken, pigment transfer immediately followed. Ultramarine blue had the greatest pigment transfer, whereas cadmium red had slightly less, and titanium white had minimal color pickup. Increasing the pH of the alkaline solutions (7.5–8 to 10–12) showed greater pigment transfer and sensitivity of the acrylic emulsion paint films.

After varnish removal from the paint samples, changes in color and gloss were greatest for ultramarine blue, followed by cadmium red, and least for titanium white; often, the UVA-aged samples showed the greatest change because of the increased insolubility of the varnish. This varnish therefore required a stronger alkaline solution and more mechanical action during swabbing. Overall, the different alkaline solutions affected the acrylic paint color and gloss to the same degree. The SEM images were taken before and after varnish removal for only the paint samples naturally aged for 50 days, with the varnish layer left on for one month (Figure 3). All paint colors showed some changes (the surfaces were smoother), greatest for the ultramarine blue and smallest for the cadmium red. This change in surface characteristic may be related to the migration of surfactants from within the bulk film of acrylic paints onto the surface, forming crystals or layers. These surfactants can be removed during wet-cleaning treatments where water and aqueous solutions remove more material compared to nonpolar aliphatic solvents such as mineral spirits (Ormsby et al., 2006).

CONCLUSIONS

In both studies, the ultramarine blue proved to be the color most sensitive to varnish removal. In the first study, the age of the paint film and the type of solvent used proved to be important. Xylene with mineral spirits was required to remove the Soluvar

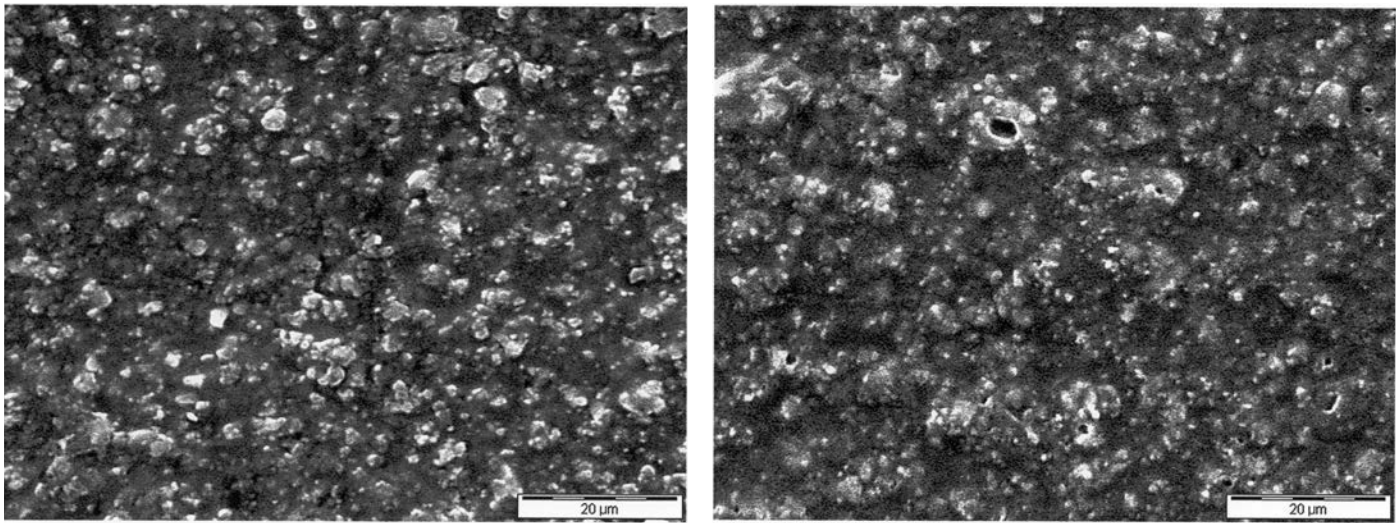


FIGURE 3. The SEM micrographs of ultramarine blue acrylic emulsion paint films naturally aged 50 days: (left) unvarnished and (right) devarnished after one month using Goldex ammonia (2500×).

varnish from the Liquitex acrylic paint samples, but this was not true for the Golden MSA varnish, which only required mineral spirits. The SEM showed no surface topography change after varnish removal for the samples examined. As expected, the sensitivity of the cured acrylic emulsion paint film significantly restricted the choice of solvents used to remove a coating; the only solvent that did not pick up color with light swabbing was mineral spirits. All paint samples were affected by repeated swabbing (two or three passes or more) with any solvent. The age of the paint film before varnishing seems to be a more significant factor than the age of the coating, but more research is needed to clarify the nature of the effect.

For the second study, which investigated the Polymer Varnish with UVLS, the UVA-exposed samples had the greatest changes, for example, in decreased ease of solubilization and often in color change after varnish removal. The alkaline solutions affected paint colors and gloss to the same degree. All reagents caused some color transfer to the swabs with repeated swabbing; pigment transfer became greater with increasing the pH of the alkaline solutions from 7.5–8 to 10–12. The samples examined by SEM showed that the surface topography was smoother after varnish removal, indicating the possible removal of surface surfactants during wet-cleaning treatments. Additionally, because the UVA-exposed samples were slightly more yellow, waterborne polymer varnishes may have a greater tendency to discolor or yellow over time in comparison to solvent-borne varnishes, therefore having a greater potential for change in the overall visual appearance of the artwork. Using alkaline reagents and aqueous cleaning methods may be beneficial to the overall health and safety of the conservator by minimizing exposure to solvents used in everyday conservation practices; however, the efficacy of using alkaline reagents to remove varnish from acrylic paintings is still questionable because of the inherent sensitivity of acrylic paint to aqueous cleaning systems and to the high pH levels that result in changes in gloss and physical properties such as swelling (Ormsby and Learner, 2009). Further work is needed on older varnishes and different removal methods for both samples and actual paintings.

Acknowledgments

The authors thank Robert Arnold, Wendy Baker, Sheina Barnes, Charles Cooney, Chelsea Elliott, Robert L. Feller, Mark Golden, Alan Grant, Debra Daly Hartin, James Hayes, Barbara Klempan, Marilyn Laver, Crystal Maitland, Helen McKay, Bronwyn Ormsby, Anthony Porter, Allison Rutter, Patrick Sabourin, Sarah Sands, Geneviève Saulnier, H. F. Shurvell, Jane Sirois, and the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

Cyr, M.-C. 2007. Should Acrylic Emulsion Paint Films Be Varnished? Investigating the Effects of Two Proprietary Coatings. Research project report. Kingston, Ontario, Canada: Art Conservation Program, Queen's University.

Golden Artist Colors, Inc. 2006. Product Information Sheet, MSA Varnish. http://www.goldenpaints.com/technicaldata/msavar.php#tech (accessed September 2006).

Jablonski, E., T. J. S. Learner, J. Hayes, and M. Golden. 2003. Conservation Concerns for Acrylic Emulsion Paints. *Reviews in Conservation,* 4:3–12.

Learner, T. J. S. 2004. *Analysis of Modern Paints*. Research in Conservation. Los Angeles: The Getty Conservation Institute.

Min, E. 2009. To Varnish or Not to Varnish: An Investigation of the Removability of a Proprietary Varnish from Acrylic Emulsion Paint Films. Research project

report. Kingston, Ontario, Canada: Art Conservation Program, Queen's University.

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.

Ormsby, B. A., T. J. S. Learner, G. M. Foster, J. R. Druzik, and M. R. Schilling. 2006. "Wet Cleaning Acrylic Emulsion Paint Films: An Evaluation of Physical, Chemical and Optical." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. W. Krueger, and M. R. Schilling, pp. 189–200. Los Angeles: The Getty Conservation Institute.

Quillen Lomax, S., and S. L. Fisher. 1990. An Investigation of the Removability of Naturally Aged Synthetic Picture Varnishes. *Journal of the American Institute for Conservation,* 29(2):181–191. http://dx.doi.org/10.2307/3179582.

Samet, W., ed. 1998. *Painting Conservation Catalog*. Volume 1, *Varnishes and Surface Coatings*. Washington, D.C.: The Paintings Specialty Group of the American Institute for Conservation of Historic and Artistic Works.

Smithen, P. 2007. "A History of the Treatment of Acrylic Painting." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. W. Krueger, and M. R. Schilling, pp. 165–174. Los Angeles: The Getty Conservation Institute.

Extended Abstract—Cleaning Issues for Nine Francesc Artigau Pop Art Paintings

Anna Nualart-Torroja, Marta Oriola-Folch, and Marina Mascarella-Vilageliu

INTRODUCTION

In the 1960s, Pop artist Francesc Artigau (born in Barcelona, 1940) painted a series of nine works on plywood panels using a traditional primer of commercial gouache, egg yolk, and color pencils. After more than 30 years of exposure to rubbish amidst an indeterminate number of dogs, the paintings show a deplorable state of conservation. The present study examines the treatment undertaken on the paint and ground layers, consisting mostly of cleaning, one of the key challenges of the project (Figure 1).

MATERIALS AND METHODS

The recently restored birch plywood supports (Nualart et al., 2010) had undergone a process of tremendous deterioration due to humidity from the ground and dog urine as well as from nonprofessional attempts at cleaning the works. The paint and ground layers also suffered from the effects of paint loss, damp spots, loss of cohesion of materials, fungi, grime embedded into all levels, erosion, and traces from cleaning tools.

The painting technique used by the artist was commercial gouache (Talens) mixed with egg yolk, applied on a traditional ground layer made of rabbit skin glue and calcium sulfate, on which the author had made a graphite and colored pencil drawing. Once the painting was finished, it was burnished with an agate stone, and no varnish coat was applied. Apart from the information currently provided by the artist, compositional and stratigraphic analyses were undertaken to identify the materials as well as the microorganisms that developed on them.

In the paint and ground layers of each of the works, pH was measured on the different colors and in different areas. A total of 171 points were measured using a CRISON pH25 pH meter, and 297 samples were analyzed using the cold extraction method with a HACH pH meter using a stainless-steel microprobe. The pH measurements are carried out to detect whether changes in the pH of materials correspond with differences in the solubility of the areas analyzed due to the ionization of binder proteins (rabbit skin glue and egg yolk). It is known that proteins are amphoteric and that at their equilibrium pH, called the isoelectric point, they have their minimum solubility (Wolbers, 2000:20).

The amount of data compiled precludes a thorough analysis in this abstract, but it can be highlighted that the difference between the surface and cold extraction pH values

Anna Nualart-Torroja, Marta Oriola-Folch, *and* ***Marina Mascarella-Vilageliu****, Fine Arts Faculty, University of Barcelona, Pau Gargallo 4, 08028 Barcelona, Spain. Correspondence: Anna Nualart-Torroja, anualart@ub.edu; Marta Oriola-Folch, martaoriola@ub.edu; Marina Mascarella-Vilageliu, mmascarella@ub.edu.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

FIGURE 1. Detail showing the deterioration present on painting H3077. Painting size: 75×75 cm.

FIGURE 2. Detail showing the agar cleaning effects (upper part of the photo) on painting H3010. Painting size: 125.2×75.2 cm.

is considerable. For the surface method, the pH values are almost two points more acidic than those obtained by the cold extraction technique, and although both methods of measurement are considered suitable, it would seem that the cold extraction method is the more reliable of the two (Saverwyns et al., 2002; Stirlič et al., 2004).

Cleaning of the paintings was carried out using a combination of dry systems (eraser dust lightly spread over the paint surface and gently suctioned off) in the areas where the material has good cohesion and a wet system applying rigid agar gel to all the paint surface. So as not to ionize the proteins during the cleaning process the agar gel was prepared with water buffered to a pH of 5.5 (Figure 2).

Agar was chosen after taking into consideration the components of both the dirt on the paint surface and the paint layer itself, both of which were water soluble. Agar's rigid structure allows the water needed in the cleaning process to be in contact with the dirt on the surface while being retained within a gelatinous structure, thus ensuring the paint layers are not impregnated. It has the additional advantage of not needing to be rinsed afterward as its rigid structure does not leave any residues.

It has been impossible to remove all of the soiling adhered to the paintings by the applied cleaning process because of the degree to which dirt had been absorbed into the strata and the fragility of the ground and paint layers, which does not allow a differentiated treatment of grime, as this could mean risking the integrity of the original components. It must be accepted that some of the dirt embedded in the paintings over the years has become part of its composition.

Given the fragility of certain areas that have suffered the direct impact of degrading elements, a consolidation of the paint layer was chosen after cleaning. Tests were carried out with 1.5% (w/v) of Jun-Funori in distilled water and with 2% (w/v) of Klucel E (hydroxypropyl cellulose) in absolute ethanol. The latter option was selected because applying a consolidant with an alcoholic vehicle appeared to be a better means of avoiding new fungus colony proliferations.

Acknowledgments

The authors thank the artist for his availability, the Museum of Hospitalet for the facilities offered in researching works from its collections, the Generalitat de Catalunya for the financing provided in its 2008 official funding for the restoration of heritage, and the University of Barcelona for granting a precompetition research project in 2009. Our gratitude also goes to Iris Bautista, Carmen López, and Teresa Sánchez, grant-funded students for this project.

REFERENCES

Nualart, A., M. Oriola, and M. Mascarella. 2010. "The Challenge of a Non-invasive Restoration of 9 of Francesc Artigau's Paintings on Plywood Supports." In *XII Reunió Tècnica: Vers una conservació-restauració sostenible,* pp. 185–199. Barcelona: Grup Tècnic, Associació Professional de Conservadors-Restauradors.

Saverwyns, S., V. Sizaire, and J. Wouters. 2002. "The Acidity of Paper: Evaluation of Methods to Measure the pH of Paper Samples." In *Preprints ICOM-CC 13th Triennial Meeting, Rio de Janeiro*, ed. R. Vontobel, Volume 2, pp. 628–634. London: James & James.

Stirlič, M., J. Kolar, D. Kočar, T. Drnovšek, V. S. Šelih, R. Susič, and B. Pihlar. 2004. What Is the pH of Alkaline Paper? *e-Preservation Science,* 1:35–47.

Wolbers, R. 2000. *Cleaning Painted Surfaces: Aqueous Methods*. London: Archetype Publications.

Rigid Gels and Enzyme Cleaning

Paolo Cremonesi

ABSTRACT. Hydrolytic enzymes and polysaccharide-based rigid gels represent two very helpful cleaning tools for a variety of polychrome artworks: moveable paintings, wooden polychrome sculptures, paper and library materials, and in some instances mineral or inorganic supports. In addition, they can be used for other tasks that are not, strictly speaking, the cleaning of a painted surface, but rather more structural interventions, such as the removal of aged film formers, such as adhesives and consolidants. Rigid gels have several advantages over conventional fluid gels, such as delivering water or aqueous solutions in a controlled way, being able to draw into their mesh any particles dissolved upon their application, and generally not requiring posttreatment rinsing. Hydrolytic enzymes, by acting selectively on specific substrates under mild conditions, can often represent a valid alternative to conventional acids and alkalis that is safer to the artwork and less hazardous to the conservator's health. Many successful applications have been conducted; however, a systematic study still remains to be done, with the aim to better understand the influence of various parameters that affect the enzyme activity and how they can be tailored to the specific needs of the artwork. The information we currently rely on is too often related to the biochemical and biological fields, rather than to the materials of the artworks.

INTRODUCTION

Water can be, depending on the situation, either a desirable or a strictly necessary medium for the cleaning of objects. The aqueous approach, originally developed by Wolbers (2000) over the past 30 years, can often be a successful alternative to the use of more toxic and less selective organic solvents for removing varnishes and overpaints, and it is strictly necessary for surface cleaning polychrome artifacts.

Water, by itself, can be a physical solvent for hydrophilic film-forming materials, but it also possess the unique feature of being a good medium for chemical reactions to occur, namely, ionization and/or dissociation of materials, i.e., acidic or alkaline film formers, or even hydrolysis. Furthermore, water is the right environment for two processes: chelation and emulsification or detergency. However, water has a potentially dangerous action on a painted surface: although exhibiting a limited action on the actual surface, it has high diffusion and capillarity, which can exert undesirable effects on materials within the internal layers of a painting.

Increasing the viscosity of water by means of hydrophilic polymers, the so-called gelling agents, is the strategy most commonly used to limit the amount of water released, particularly when dealing with water-sensitive materials and layers. Many different polymers have been used for this purpose: the well-known cellulose ethers like Klucel, the

***Paolo Cremonesi**, Cesmar7–The Centre for the Study of Materials for Restoration, Via Lombardia 41/43, 35020 Saonara, Italy. Correspondence: paolocremonesi57@gmail.com.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

pseudoplastic xanthan gum (i.e., Vanzan NF-C), and the high-viscosity polyacrylic acid derivatives (Carbopols and Pemulens).

A common feature is the need of a clearing rinse after the gel has been applied and removed with a dry cotton swab. The clearing rinse uses water to ensure proper removal of the hydrophilic gelling agents' residues. On particularly fragile surfaces, this final rinse could create a problem, considering that the gel had originally been selected just to avoid the use of free water. To avoid the drawback of these conventional fluid gels, the so-called rigid gels have been used, with the great advantage that, in general, they do not require an after treatment because of their physical form and their limited adhesive strength.

RIGID GELS

In 2003, the use of rigid agar gels was introduced by Richard Wolbers during one of his cleaning courses organized in Italy. Preliminary applications onto painted surfaces seemed very promising, and it was decided to further study their use on paintings, from both an analytical and a practical point of view (Campani et al., 2007).

At a later time, the field of study was broadened to other artifacts, such as wooden objects, plaster sculptures, and mural paintings (Anzani et al., 2008). Parallel to this study, the Istituto Centrale per il Restauro e la Conservazione del Patrimonio Archivistico e Librario (ICPAL) in Rome developed applications of similar gelling materials more suited to paper and library materials (Iannuccelli et al., 2004; Iannuccelli and Sotgiu, 2009). The latter area has grown in importance, and our separate experiences have merged into a common effort: in 2009 Cesmar7 started a joint research program with colleagues from ICPAL in Rome, the Università degli Studi in Parma, and the Opificio delle Pietre Dure in Florence that has already produced some interesting results, such as the "Study Day on Aqueous Rigid Gels" (Gel rigidi acquosi nel restauro) held in Rome on 16 June 2010.

The structure and chemistry of agarose and agar have been described elsewhere (Armisén and Galatas, 2000; Campani et al., 2007); here it is simply recalled that the polysaccharide complex agar, composed of galactose, dissolves in hot water above 85°C; once the solution is cooled below 37°C–39 °C, the polymer molecules tightly assemble into a regular mesh, capable of retaining a large amount of water, forming a so-called rigid gel. When applied to a porous surface, the gel can gradually release this water, a physical process termed syneresis.

Generally, concentrations of 2–5 g of agar in 100 mL of water are used, depending upon the type of application and the sensitivity to water by the treated object. Different varieties of agar are commercially available, ranging from laboratory to food additive grades, and in our experience all types tested performed in a very similar way.

Agarose is the purest galactose-derived gelling material; it produces clear, more transparent gels than the clouded agar gels, a particularly important feature when treating delicate supports, such as paper. However, because of its high price (10–20 times more expensive than agar) it is unlikely to be used in conservation. Furthermore, for the specific structural characteristics of some artworks, the "poorer" agar is still to be preferred because of its slower rate of syneresis compared to agarose. Agaropectin, the other polysaccharide component of agar, is a sulfated polymer, and the bulky sulfate groups decrease the pore sizes within the polymer network, thus slowing down the discharge rate of water. Besides applications for the cleaning of surfaces, rigid agar gels in many instances can perform as true humidification systems, capable of controlled-release of water for whatever conservation purpose.

Extensive analytical testing was done on very porous model supports using gas chromatography–mass spectrometry (GC-MS). The chromatographs always showed a minute peak for galactose, indicating that only trace amounts of agar deriving from the gel had permeated into the porous supports (Campani et al., 2007).

As an example, Figure 1 shows the application of a rigid agar gel onto an eighteenth-century polychrome wooden cross, painted in egg-tempera medium, from the Balkan area. The whole surface had been coated with a pigmented layer of animal glue, now strongly altered and discolored. Water was necessary for its removal, and the safest way of using it could only be in gel. However, even with thick Carbopol gels, the rinsing phase affected the paint layer because of the presence of some very hydrophilic components within the paint layer, likely a polysaccharide gum additive. A rigid agar gel, applied for just 1–1.5 minutes, delivered the right amount of water to swell the proteinaceous material, which was then completely removed by the simple action of a dry cotton swab.

FIGURE 1. Application of a rigid agar gel to a tempera-painted wooden cross to remove a discolored proteinaceous coating.

According to the requirements of the specific treatment, the gel may be left on for a limited time, until the amount of water necessary to obtain the desired results has been released or until the water has been totally "discharged." In the latter situation, what remains is a solid crust, which is easy to remove because it does not adhere to the surface. Observation of the gradual coloring of the gel as it absorbs the dissolved materials is often used to verify its action. Concentration gradients, once water from the gel starts diffusing into the surface materials, can be hypothesized as the main factor controlling this process.

In other cases, the surface material will not completely dissolve, such as when intrinsically hydrophilic substances gradually lose this characteristic upon aging and oxidation or when they cross-link with other materials. Then the usefulness of the gel may be identified by the swelling of the material, enough to soften it and aid its removal with a bland mechanical action. This type of action does entail treatment subsequent to gel application, but certainly to a far lesser degree than the washing procedure required when using traditional gels made from cellulose ethers or polyacrylic acid, which tend to adhere to the surface.

If, instead of simply gelling water, an aqueous solution containing acids or bases, chelating agents, or surfactants is used, a more specific action on certain materials can be obtained, such as (1) ionizing acid or basic substances (animal glues; certain polysaccharides, especially when aged; and lipophilic materials, such as natural resins, oils, waxes, especially when aged and/or oxidized), by using bases or acids, (2) dissolving insoluble salts (such as surface patinas composed of salts of fatty acids on oil paintings or caseinates) by using chelating agents such as citrates or EDTA (ethylenediaminetetraacetic acid) salts, and (3) emulsifying or dispersing hydrophobic materials, both oily and fatty (oils and natural resins), by using surfactants. Regarding their conservation, it must be remembered that these gels are aqueous-based materials and therefore have a tendency to develop mold. This requires a minimum of care during preparation (clean glassware), particularly when handling, to avoid contamination of the fresh gel (use of gloves, clean implements, etc.). The gel blocks may be stored in a refrigerator after sealing their surface with a plastic membrane for further protection.

The nature of these rigid gels also represents the main limit to their use: since they are rigid, it may be difficult to obtain good contact on surfaces that are not perfectly flat, even if the gel thickness is decreased. This problem stimulated our curiosity: might a different application method for the agar be developed that would allow it to be distributed over the irregular surfaces of three-dimensional objects, terra-cottas, plaster objects, and marble sculptures? On the basis of preliminary applications on plaster sculptures at the Galleria d'Arte Moderna in Milan, a new procedure was developed: once agar has dissolved in water at the proper melting temperature, the solution is cooled down to only 40°C–45°C, so that a semisolid state is achieved, allowing it to be brushed onto the surface to be cleaned.

In most applications to plaster sculptures, after only three minutes the plaster appeared to be clean with only a minimum release of water into the material. In some instances, to eliminate stains penetrated into the plaster or salts, it may be useful to leave the gel on until it dries entirely. In any case, the agar film formed on the surface can then be easily removed. Depending on the specific treatments, the appropriate agar concentration range is 2.5–5 g in 100 mL of deionized water. The best results were obtained by redissolving the gel after the initial solidification, as this partially modifies it since the second heating, which is faster than the first one needed to transform the powder into gel, renders the gel more homogeneous, with better water retention properties. These applications were also monitored by Fourier transform infrared spectroscopy and GC-MS analysis; the results again indicate that only trace amounts of agar deriving from the gel permeated into the plaster (Anzani et al., 2008). The new methodology permits cleaning plaster objects in an efficient and innovative way while remaining respectful of the porous nature of the substrates, which are potentially quite sensitive to treatment with water.

A further development that led to a broader area of application consisted of using a different kind of agar with a lower gelling temperature, i.e., 28°C–30°C. The semisolid state, required for the brush-on application, is then reached at 35°C. This lower temperature is safer for application to organic supports such as wood and canvas. For example, polychrome wood ceiling elements have been treated according to this procedure. The agar-substitute Phytagel, with a 27°C–31°C gelling temperature, is also perfectly appropriate for this type of application; furthermore, its higher flexibility and transparency in some instances represent a great improvement over agar.

HYDROLYTIC ENZYMES

Class III enzymes, according to the 1960s Enzyme Committee classification, namely, hydrolytic enzymes, or simply hydrolases, catalyze selective cleavage of specific bonds within the proper substrates. Among the hydrolases, proteases, amylases, and esterases hydrolyze peptide bonds (-CO-N-) in proteins, α-1,4-glucosidic bonds (-O-C-O-) in starch, and ester bonds (-CO-O-) in simple and complex esters, respectively (Nelson and Cox, 2009). The most typical feature of enzymes is the molecular recognition of the proper kind of substrates, i.e., the one most similar to the structure of the active site of the enzyme, and selectivity results from this feature that is unmatched by more conventional reagents, such as acids and alkalis, or even by organic solvents.

Since the 1970s, these enzymes have found application in conservation treatments (Bellucci and Cremonesi, 1994; Buttazzoni et al., 2000; Wolbers, 2000; Cremonesi, 2002, and references therein) for the removal under controlled conditions of such film-forming materials as animal and fish glues and gelatins, albumin, and casein; starch and starch-containing materials, e.g., flours; vegetable glues; drying oils; fats; some waxes; and some ester-containing synthetic resins (Bellucci et al., 1999).

When these film formers become largely insoluble in water (for hydrophilic materials) or in organic solvents (for lipids),

upon aging, a chemical action is required for their removal. If ionization or dissociation carried out by acids and alkalis under moderate-pH conditions (about 5–9 for polychrome surfaces) is not sufficient, the same acids or alkalis must be used under hydrolytic conditions, i.e., higher concentration, higher pH, and longer application times, with a greater risk to the artwork's integrity. In these cases, the hydrolytic action of enzymes can be a more effective and safer alternative.

Figure 2 illustrates a representative enzyme application. A small polychrome stone sculpture showed a strongly discolored appearance, caused by the alteration of materials that had been repeatedly applied over it for consolidation and outdoor protective purposes as well as for "brightening up" the colors. With aging, these mixed materials had become intractable: among traditional methods, only concentrated ammonia solutions could remove them, yielding a very blanched and abraded surface.

FIGURE 2. Application of an enzyme solution, absorbed onto a cellulose tissue, on a polychrome stone sculpture to remove a discolored oily and proteinaceous coating.

After characterizing the materials by GC-MS as linseed oil and animal glue, a bacterial lipase, effective at a pH of 7–7.5, and a bacterial protease, with an optimal pH of 7.5, were chosen. Free-enzyme solutions, containing 0.5–1 g enzyme in 100 mL of 50 mM phosphate buffer, were applied in sequence onto the surface, supported on pure cellulose tissues, kept in contact with the surface, and warmed to about 35°C for 15–20 minutes. After this, the tissues were removed, and the surface was cleared with artificial saliva (freshly prepared by dissolving at 37°C 0.1 g mucin in 100 mL of distilled water). It is important to stress that for an enzymatic treatment cleaning is carried out in an aqueous medium within a "safe" pH range and in a basically nontoxic environment (if precautions are taken to avoid skin contact and inhalation of the enzymes in the powder form and skin contact once the solutions are made.)

Enzymes have been used, depending on the circumstances, as free solutions, absorbed on tissues, or in a gelled form. Solutions may also be gelled with agarose and agar since the dimensions of the pores in the gel network structure are large enough to even allow movement of the enzyme protein macromolecules. To use them this way, however, it is necessary to slightly vary the preparation procedure because enzymes are thermolabile: the rigid gel is prepared as already described, but using only two-thirds the prescribed amount of water; the remaining one-third, buffered to the correct pH, will be used to prepare the enzyme solution. The latter is then quickly mixed into the cooling agar solution once its temperature is down to 45°C–50°C.

Many enzymatic applications in cleaning treatments have been carried out throughout the years on different kinds of objects (paintings on canvas and panel, mural paintings, paper artifacts, stone sculptures), yielding in general good results. In all instances, the enzymatic treatment was chosen precisely because more conventional materials were either too slow or produced unsatisfactory results from the point of view of the visual appearance (incomplete removal, not homogeneous, blanched, etc.) or required conditions that were deemed risky to the structural integrity of the artwork (excessive polarity or pH, too long an application time, limited selectivity) and/or were hazardous to the conservator's health.

However, our understanding of how hydrolases work on artifacts is still largely incomplete, and there is need for a systematic study. Far too much of the information available is taken from the biochemical and biological fields and is simply considered valid and applicable to the conservation field as well. However, in many cases, this is only a rough approximation.

In a biological system the catalytic process is very efficient. When enzymes are taken out of their biological "protective" environment and used as mere chemical reagents, e.g., when applied to the surface of artworks for cleaning purposes, a large part of this efficiency is lost. Optimal reaction conditions, such as pH and temperature, may not be used for cleaning conditions, and furthermore, inhibitors may be present on the artwork, such as salts, metal ions, or other molecules that, by binding to the proteinaceous structure of the enzyme, induce changes in its

conformation. These changes may bring about a decrease in or even the total loss of the enzymatic activity.

For instance, heavy-metal ions, such as lead, mercury, antimony, and cadmium, are known to be powerful enzyme inhibitors under homogeneous phase catalysis, i.e., when they are in the form of salts, dissolved in the same aqueous medium as the enzyme. These same metals are found within many ancient pigments, for example, lead white, minium, orpiment, and cinnabar, just to mention a few. However, when part of a paint layer, particularly an oil-bound layer, these metal ions may be not bioavailable to the enzyme if the pigment particles are fully coated by a binder film. Therefore, under these circumstances, they may not exert enzyme inhibition.

CONCLUSIONS

Rigid agar gels have proven suitable conservation tools for treating various kinds of objects: for cleaning soiled surfaces and, when applied still in a semisolid state, even for soiled objects. Acting as "molecular sponges," these gels can draw into their tight polymer mesh the particles dislodged from the surface and generally require no posttreatment rinsing.

When gels are used over the hydrophilic film-forming materials to be removed, simply varying the application time allows the transfer of the proper amount of water and swelling of the material to the point that removal can then occur by gentle mechanical action. In this fashion, rigid gels are most useful on the verso of paintings, when residual lining adhesive has to be removed with a limited amount of water, and on paper.

These treatments are safe for the artwork. Analytical studies have revealed that only trace amounts of polysaccharides are transferred into the porous objects treated with agar gels.

Hydrolytic enzymes represent powerful means for tackling difficult tasks in cleaning, minimizing the risk for the artwork: in an aqueous medium under mild-pH conditions, aged, insoluble protein-based film-forming materials, starch-based glues, and oil-bound overpaints can often be effectively removed with proteases, amylases, and esterases, respectively. Many successful treatments have been conducted on various supports, and the enzyme's catalytic action has been assisted and monitored by analytical techniques. However, a systematic study of how hydrolytic enzymes work on artworks remains to be carried out, with a focus on optimizing the parameters that are crucial to catalytic activity in relation to the materials that are present on the artwork.

REFERENCES

Anzani, M., M. Berzioli, M. Cagna, E. Campani, A. Casoli, P. Cremonesi, M. Fratelli, A. Rabbolini, and D. Riggiardi. 2008. *Gel rigidi di agar per il trattamento di pulitura di manufatti in gesso—Use of Rigid Agar Gels for Cleaning Plaster Objects*. Translation by D. Kunzelman. Quaderni Cesmar7, No. 6. Padua: Il prato.

Armisén, R., and F. Galatas. 2000. "Agar." In *Handbook of Hydrocolloids*, ed. G. O. Phillips and P. A. Williams, pp. 22–40. Boca Raton, Fla.: CRC Press.

Bellucci, R., and P. Cremonesi. 1994. L'uso degli enzimi nella conservazione e nel restauro dei dipinti. [The Use of Enzymes in the Conservation and Restoration of Paintings.] *Kermes, arte e tecnica del restauro*, 21:45–64.

Bellucci, R., P. Cremonesi, and G. Pignagnoli. 1999. A Preliminary Note on the Use of Enzymes in Conservation: The Removal of Aged Acrylic Resin Coatings with Lipase. *Studies in Conservation*, 44(4):278–281. http://dx.doi.org/10.2307/1506657.

Buttazzoni, N., A. Casoli, P. Cremonesi, and P. Rossi. 2000. Preparazione e utilizzo di gel enzimatici, reagenti per la pulitura di opere policrome. [Preparation and Use of Enzymatic Gels as Reagents for the Cleaning of Polychrome Objects.] *Progetto Restauro*, 16:11–19.

Campani, E., A. Casoli, P. Cremonesi, I. Saccani, and E. Signorini. 2007. *L'uso di agarosio e agar per la Preparazione di "gel rigidi"—Use of Agarose and Agar for Preparing "Rigid Gels"*. Translation by D. Kunzelman. Quaderni Cesmar7, No. 4. Padua: Il prato.

Cremonesi, P. 2002. *L'uso degli enzimi nella pulitura di opere policrome*. [The Use of Enzymes in Cleaning of Polychrome Works.] 2nd ed. I Talenti 4. Padua: Il prato.

Iannuccelli, S., and S. Sotgiu. 2009. "L'impiego di gel rigidi polisaccaridici per il trattamento di pulitura di opere grafiche a stampa." [The Use of Polysaccharide Rigid Gels for the Cleaning Treatment of Prints.] In *Lo stato dell'arte: Proceedings of the 7th National Congress Italian Group of the International Institute for Conservation*, pp. 1–8. Turin, Italy: IGIIC Gruppo Italiano.

Iannuccelli, S., S. Sotgiu, and M. Missori. 2004. "La chinea di Papa Clemente VIII del 1598: Pulitura del supporto cartaceo, tecniche di lavaggio e diagnosi ottica dei risultati." [The White Horse of Pope Clement VIII from 1598: Cleaning of the Cardboard Support, Washing Technique and Visual Diagnosis of the Results.] In *Lo stato dell'arte: Conservazione e Restauro, Confronto di Esperienze; Proceedings of the 2nd National Congress Italian Group of the International Institute for Conservation*, pp. 124–135. Turin, Italy: IGIIC Gruppo Italiano.

Nelson, D. L., and M. Cox. 2009. *Lehninger Principles of Biochemistry*. 5th ed. New York: W. H. Freeman.

Wolbers, R. C. 2000. *Cleaning Painted Surfaces: Aqueous Methods*. London: Archetype Publications.

Effects of Commercial Soaps on Unvarnished Painted Surfaces: A Pilot Study for Their Assessment

Andrés Sánchez-Ledesma, Carmen Muro-García, and María Dolores Gayo-García

ABSTRACT. The elimination of soiling from painted surfaces, especially for recent unvarnished paintings, by means of alkaline soaps with a high pH poses a significant risk to the objects. The wide range of objects that can be treated with these products and their long-standing presence on the specialist market have led to this pilot study to evaluate the existence of residues and/or damage from them on painted surfaces. The methodology applied involves the use of analytical techniques such as gas chromatography–mass spectrometry, Fourier transform infrared spectroscopy, polarized light microscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy, and confocal scanning microscopy. This study presents the results from the use of Vulpex soap at low concentrations in an aqueous solution, in white spirit, and in fluid hydroxypropyl cellulose gels, applied directly on the unvarnished painting or on barrier paper and rigid agar gels. A reduction in the amount of residues was observed when soap was used in a 1% concentration in white spirit or as a gel. All the aqueous treatments caused surface damage, especially cracking, flattening, and particle removal and accumulation. The damage may be associated with both the application method and the rinsing process. Some treatments have been tested by a team of professional restorers, and a good correspondence was found with the results from the test samples. The main difference between restorers appears to depend on the area of the painting that was treated.

INTRODUCTION

The wide range of pictorial techniques and finishes employed in paintings held at the Museo Thyssen-Bornemisza, Museo Nacional Reina Sofía, and Museo Nacional del Prado has prompted the need for a far-reaching study of commercial products recommended for the cleaning of paintings and sculptures. This project received the support of several companies specializing in the distribution of restoration materials, which will later publish the results from this pilot study. Because of the large number of restorers who will have access to the results of these studies through these companies, the project also included products that are not in widespread use in museum cleaning protocols but that may present a high risk for restoration processes in general.

The first aim of the project was to develop an analysis methodology that allowed assessment of potential damaging effects on the pictorial surface by the commercial products and to monitor the residues after cleaning. Within the Spanish market there are several recommended commercial cleaning products, including alkaline soaps, resin soaps, and products formed by a complex mixture of surfactants and other additives, such as Vulpex, resin soap 1194, resin soap 1295, Contrad 2000, and "concentrado aniónico."

***Andrés Sánchez-Ledesma**, Museo Thyssen Bornemisza, Paseo del Prado 8, 28014 Madrid, Spain. **Carmen Muro-García**, Museo Nacional Centro de Arte Reina Sofía, Calle Santa Isabel 52, 28012 Madrid, Spain. **María Dolores Gayo-García**, Museo Nacional del Prado, Calle Ruiz de Alarcón 23, 28014 Madrid, Spain. Correspondence: Andrés Sánchez-Ledesma, asanchezledesma@artelab.es; Carmen Muro-García, carmen.muro@mcu.es; María Dolores Gayo-García, dolores.gayo@museodelprado.es.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

In some cases, the pH value in the diluted solutions of these materials is high, so the risk to paintings treated with these systems, especially unvarnished ones, is consequently also high.

Several studies have been performed to optimize cleaning systems by adding various thickeners to reduce the hazardous effects of solvents and aqueous solutions on vulnerable surfaces (Wolbers, 2000:74–84; Cremonesi, 2004; Campani et al., 2007; Anzani et al., 2008; Sánchez-Ledesma et al., In press). Furthermore, other studies have been carried out to quantify the residues and their potential effects on the paint layers (Bueno et al., 2004; Stulik et al., 2004).

Some tests have shown that the use of barrier paper between the gelled system and the painted surface may provide another alternative to protect the paint against damage from cleaning interventions (Sánchez-Ledesma et al., 2008b). But this requires great skill to ensure the joints between the different applications are unnoticeable; therefore, it is more efficient for local use.

Since the 1970s, Vulpex soap has been recommended for the field of restoration. Vulpex is manufactured only by Picreator Enterprises Ltd. (London), who have the registered trademark (Conservation by Design, 2005; Ross and Phenix, 2005). It is an alkaline soap, described as potassium methylcyclohexyl oleate.

It was not until some years later that the risk that this material posed for painting cleaning was mentioned (Carlyle et al., 1990; Southall, 1990; Osete-Cortina and Doménech-Carbó, 2005). The erosion that an aqueous solution of Vulpex with a pH value of 11.2 caused on a varnished painting was reported by Burnstock and White (1990). Similar effects were later observed on artificially aged paintings, so the authors recommended the use of diluted solutions followed by a double rinsing of the surface to diminish the risk from this product (Ross and Phenix, 2005). Recent preliminary studies have shown the presence of Vulpex residues and damage on the surface of test samples from young unvarnished paintings with 1% aqueous and 2.5% white spirit solutions (Sánchez-Ledesma et al., 2008a, 2009).

The long history and permanence of Vulpex in the specialist market suggested the need to complement the available information with studies that included other theoretically safer methods for the application of soap on a vulnerable support such as unvarnished paintings. These methods involve mixing the soap with a hydroxypropyl cellulose fluid gel (Klucel G) that is applied on Japanese paper acting as a barrier and on an agar rigid gel. The work with this model can be used as a reference to study other commercial soaps in the specialist market. The effect of applying and rinsing the different systems has also been evaluated with a group of professional restorers. The results of this study, including references from previous research, were sent to distributors for their incorporation into the technical files. This study is completely free of commercialism by the authors and the distributors of materials who have supported it.

MATERIALS AND METHODS

Experimental Paint Surfaces: Test Samples

Tests were carried out on two different paintings: P1 and P2. P1, an oil painting with 10 years of natural aging and no historic or artistic value, was used for all experimental tests. The size of each test sample was 1 × 2 cm for the analysis by polarized light microscopy, scanning electron microscopy (SEM), gas chromatography–mass spectrometry (GC-MS), and Fourier transform infrared spectroscopy (FTIR) and 2 × 2 cm for the confocal scanning microscopy (CSM) analyses.

P2 is a 1958 oil painting from a private collection (obtained specifically for this study) used by the professional restoration team for treatment tests. This painting had a seemingly uniform layer of dirt on its entire surface. It was divided into 24 sections by means of a water mark, and the various cleaning treatments were applied on the different sections (Table 1).

TABLE 1. Cleaning systems. V = Vulpex; W = water; WS = white spirit; FG = fluid gel; FGP = fluid gel applied on barrier paper; RG = rigid gel.

Cleaning system	Description	Paintings
VW 0.5%	Aqueous solution of Vulpex at pH 10.5	P1
VW 1.0%	Aqueous solution of Vulpex at pH 11.2	P1
VW 5.0%	Aqueous solution of Vulpex at pH 12.2	P2
VWS 1.0%	Vulpex in white spirit in concentrations of 1.0 % (v/v)	P1, P2
VWS 5.0%	Vulpex in white spirit in concentrations of 5.0% (v/v)	P1
VFG 1.0%	Aqueous solution of Vulpex at pH 11.2 gelled with hydroxypropyl cellulose (Klucel G) with a 3% concentration that resulted in a fluid gel; this gel was applied directly on the painting surface	P1
VFGP 1.0%	Aqueous solution of Vulpex at pH 11.2 gelled with hydroxypropyl cellulose (Klucel G) with a 3% concentration that resulted in a fluid gel; this gel was applied on a barrier Japanese paper	P1, P2
VRG 1.0%	Aqueous solution of Vulpex at pH 11.2 gelled with agar with a 3.5% (w/v) that resulted in a rigid gel	P1, P2

The aqueous and organic solvent solutions were applied with a swab to the painting surface. Cotton swabs, partially immersed in the solution and blotted, were rolled over the painting surface 10 times using minimal pressure and no rubbing action. The rinsing was done with the same method, using deionized water or white spirit, depending on the soap solvent.

The fluid gel that was applied directly on the painting was left for a minute and was then removed with a dry swab. A swab that was moist with water was then used for rinsing. Whenever the gel was applied on the Japanese paper used as a barrier it was left for two minutes on the painting surface. The paper was then removed and the painting was rinsed with a swab that was water moistened.

The rigid gel was used in accordance with the specifications presented by Cremonesi and Borgioli (2008) in a workshop at the Museo Nacional Reina Sofía: a section the size of the area to be cleaned was cut and placed directly on the painting for two minutes and then removed, and a clear gel was used for rinsing. This operation was repeated twice.

In addition, water and a rigid agar gel without soap were applied to evaluate the effect of these components on the surface of the test samples. The same methodology and treatment times as in the case of solutions and gels that included Vulpex were applied. The test samples were left to dry at ambient temperature for two weeks before analyses to determine potential residues and surface alterations were performed.

Residue Studies

GC-MS

Analyses by means of GC-MS were carried out applying the technique used frequently for the identification of fatty acids in paint layers. Microsamples were taken and transferred to a 1 mL vial, and 15 μL of methanol and 15 μL of the 0.2 N methanolic (m-trifluoromethylphenyl) trimethylammonium hydroxide (Meth Prep II) derivatization reagent were added. Ultrasound was applied for 15 minutes, and the samples were then placed at 60°C for three hours. Later, 0.2 μL were injected in splitless mode into the GC-MS (further details on the operating conditions can be found in Appendix A).

The presence of Vulpex residues was estimated by detecting methyl palmitoleate and the increase in methyl oleate in the treated samples. The ratios between the oleate/stearate (O/S), oleate/palmitate (O/P), palmitoleate/stearate (PO/S), and palminoleate/palmitate (PO/P) methyl esters were calculated on the basis of the integrated area of the respective peaks.

FTIR

The FTIR analyses were performed with an attenuated total reflectance (ATR) accessory. The ATR unit was used first to identify potential residues on the surface. On some occasions it became necessary to separate microsamples or to extract them by means of an ethanol-water mixture (75:25) to perform the transmission analyses. These were done by grinding the samples in KBr in an agate mortar to prepare a 1 cm diameter pellet.

Surface pH before and after the Cleaning Treatment

The pH level was measured with a CRISON 507 pH meter, a CRISON 52-07 surface metering electrode, and buffer solutions at pH 4.01 (Testo quality 0554-2061) and pH 7.00 (Testo quality 0054-2063).

Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy

A Jeol JSM–6390 LV variable-pressure scanning electron microscope was used to examine the same area of paint surface before and after subsequent treatments. The analyses were performed on 1 × 2 cm test samples without coating. Secondary electron scanning electron microscopy (SEM) images in high vacuum mode were taken at different positions with magnifications of 30×, 100×, and 500×.

The existence of Vulpex residues on the surface of the samples was confirmed by identifying potassium by means of SEM and energy-dispersive X-ray spectroscopy (SEM-EDS). A semiquantitative analysis was performed on the samples treated with the different cleaning systems.

Surface Alteration Study

The rinsing swabs were analyzed by GC-MS to identify extracted fatty acids from the paint after the different treatments had been performed. These results were used as an indirect indicator of possible surface alterations. The dry-cleaning swabs were placed inside vials to which 1mL of methanol was then added and ultrasonicated for 15 minutes. Finally, the vials were left for 24 hours at room temperature. The extracts were transferred to new vials, dried under stream nitrogen, and derivatized for analysis after adding 1 μg of nonadecanoic acid as an internal standard. Samples of the cotton swabs were also analyzed.

CSM

Surface topography was analyzed using an optical imaging profiler (Sensofar Plm 2300) that combines the confocal and interferometry techniques. Confocal microscopy was used to build a three-dimensional structure from the recorded images. Samples were scanned vertically in steps so that the focus covered every surface point. The height of the surface at each point was found by detecting the peak of the narrow axial response.

In particular, confocal imaging was used to study the surface of a 5.86 × 4.40 mm^2 section in the center of the sample using a 10× lens. The topography was recorded twice: the original surface and then the surface after the cleaning process.

Surface roughness was characterized using the roughness average value R_a, which is defined as the average value of the absolute profile amplitude inside an evaluation length divided by the total length. The amplitude at each point is calculated as the vertical deviation of the roughness profile from the mean line. A similar definition is used when this value is used to characterize the surface roughness.

The variation percentage of R_a in each test sample was calculated with $[(R_{af} - R_{ai})/R_{ai}] \times 100$, where R_{af} corresponds to the measurement after the treatment and R_{ai} corresponds to the measurement before the treatment. Ten 1.46×1.10 mm^2 sections were considered in each sample.

RESULTS AND DISCUSSION

General Composition of the Paintings

The painting used for the test samples (P1) was made up mainly of titanium white, calcium carbonate, zinc white, ultramarine blue, and chrome green. The painting used by the restoration team for cleaning (P2) contained barium white, zinc white, and calcium carbonate in the ground layer, and the pigments identified in the paint layers were titanium white, zinc white, ultramarine blue, chrome green, red lake pigment, umber pigments, and bone black. The binding medium was linseed oil in both paintings.

Assessment of the Existence of Residues on the Painted Surfaces

The analyses of the paint microsamples and the Vulpex soap by GC-MS showed the existence of palmitic acid (C16:0), oleic acid (C18:1), and stearic acid (C18:0). The amount of oleic acid in the Vulpex was significantly greater. Furthermore, azelaic acid (2C(9)) was identified in the paintings, and palmitoleic acid (C16:1) and linoleic acid (C18:2) were found in the Vulpex.

The ratios between the different fatty acids in all the samples were calculated before and after the cleaning treatments. An increase in the amount of oleic acid and the identification of varying amounts of palmitoleic acid in the treated paintings were considered markers of Vulpex residues. In addition, the existence of Vulpex was confirmed by means of FTIR by locating the typical stress vibration of the carboxylate group at 1551 and 1566 cm^{-1} in the ATR and transmission analyses, respectively. Other bands in the 1405–1450 cm^{-1} range could not be assigned because they overlapped the bands of carbonates in the paint layers of the samples (Figure 1).

All nongelled aqueous treatments left residues of Vulpex on the surfaces. On recent paintings, alterations such as softening and erosion caused by the high pH value of these solutions probably allowed the soap to penetrate and rendered the rinsing unable to completely eliminate the product. Painting P2, which was treated with a high concentration of Vulpex in water as per the manufacturer instructions, showed a high amount of residues in

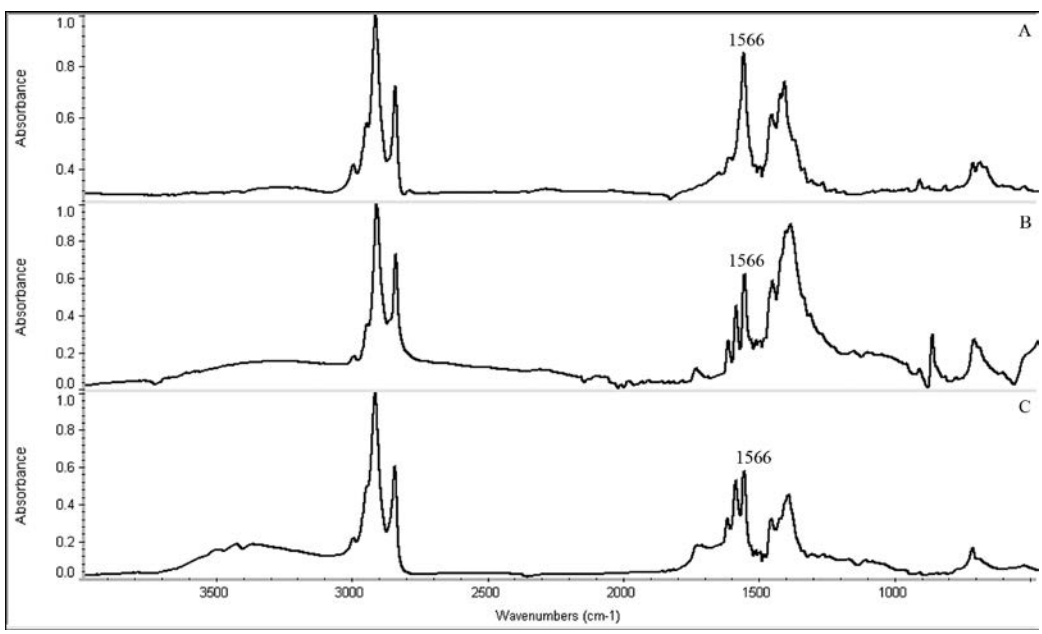


FIGURE 1. (A) The FTIR spectrum showing the 1566 cm^{-1} band from the stress vibration of the carboxylate group found in the Vulpex. The spectra obtained in samples from (B) P1 VWS 5.0% and (C) P2 VW 5.0% were taken as examples. The band at 1566 cm^{-1} was found in these samples, pointing toward the existence of Vulpex residues.

all tests. The restorers stopped the rinsing process as soon as they observed damage on the paintings, so this probably had a bearing on the widespread existence of residues.

The cleaning systems that employed a 1% concentration of Vulpex in white spirit did not leave soap residues in the samples, whereas those that employed a solution with 5% Vulpex did leave residues (Figure 2). The greater concentration of this solution has a bearing on the results, although it is also possible that rinsing only with white spirit did not completely eliminate the Vulpex, given the lower solubility of soap in hydrocarbons. Similar results were presented by Ross and Phenix (2005), thus confirming the need for rinsing with water after using white spirit, as described for other cleaning systems (Burnstock and White, 1990). Varying results were obtained in painting P2, treated with 1% white spirit by the restoration team. This case was the only one where differences in the existence of residues were encountered, probably because white spirit was not very efficient as a rinsing system.

Results were different with gelled Vulpex since no residues were found on either painting (P1 and P2). Special attention should be paid to the fact that the ratios between O/S and O/P in painting P2 were lower in treated areas than in untreated areas. The greater amount of oleic acid in untreated samples could be caused by the fatty nature of the surface dirt, as verified by the analyses of the cleaning swabs. However, the lack of palmitoleic acid in the GC-MS analyses and the stress vibration of the carboxylate group in the FTIR analyses indicate that no Vulpex soap residues could be detected with these techniques. The incorporation of techniques for the precise quantification of residues into the analysis methodology will be the next stage of this pilot study.

The reduction in the contact surface between the cleaning system and the painting, either by incorporating a thickener or applying barrier paper, confirmed a minimized penetration, facilitated rinsing, and reduced the amount of residues. It is especially significant to note that rinsing with clear agar gels resulted in a residue-free surface. This result shows great

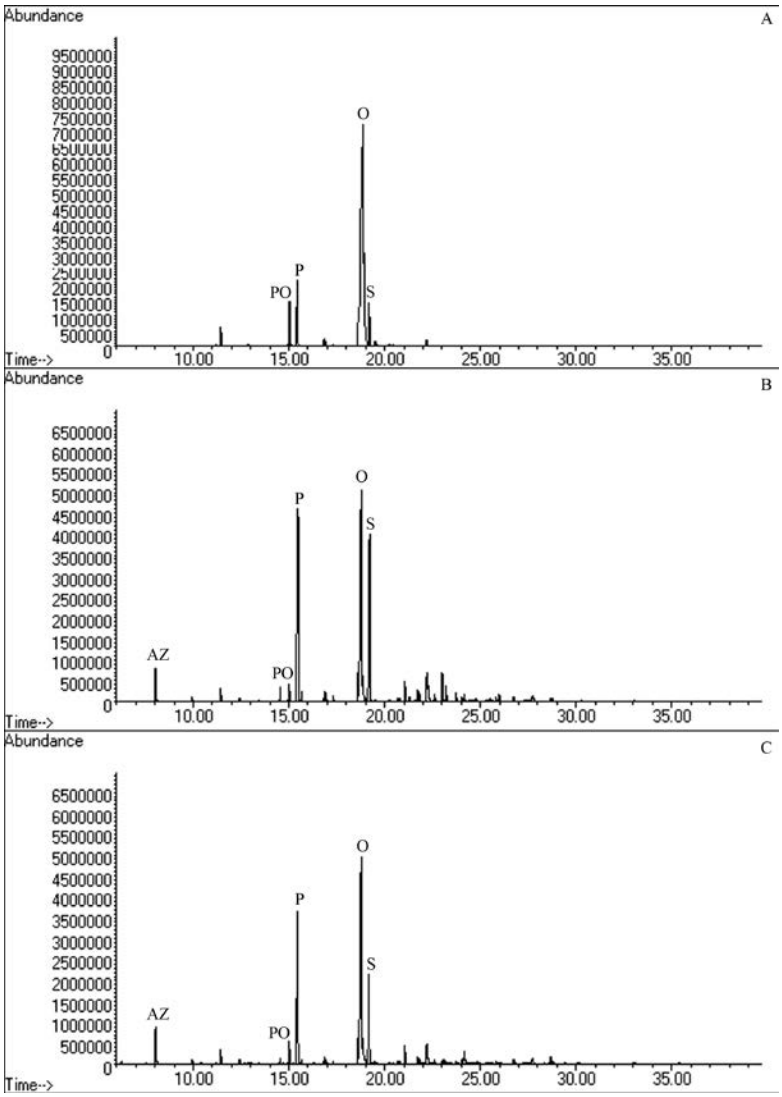


FIGURE 2. (A) Chromatogram for Vulpex, showing the peaks for methyl palmitoleate (PO), methyl palmitate (P), methyl oleate (O), and methyl stearate (S). The chromatograms of samples (B) P1 VWS 5.0% and (C) P2 VW 5.0% are included as examples. These samples show large amounts of methyl oleate and small amounts of methyl palmitoleate, which serve as markers for the identification of residues. AZ corresponds to the dimethyl azelate found in the paintings.

TABLE 2. Residue markers estimated by gas chromatography–mass spectrometry (GC-MS) and Fourier transform infrared spectroscopy (FTIR). Results in italics correspond to areas where no residues were detected, and (—) indicates that no measurements were made. CS: cleaning systems, O =: oleic acid; P = palmitic acid; PO = palmitoleic acid; S = stearic acid; V = Vulpex; W = water; WS = white spirit; FG = fluid gel; FGP = fluid gel applied on barrier paper; RG = rigid gel; FTIR (a) 1551 cm^{-1} (ATR) (b) 1566 cm^{-1} (transmission); rd = residues detected; nrd = no residues detected.

	GC-MS								FTIR-ATR (cm^{-1})		Residues	
	O/S		O/P		PO/S		PO/P					
Cleaning System	P1	P2	P1	P2	P1	P2	P1	P2	P1	P2	P1	P2
VW 0.5%	0.97	—	0.71	—	0.06	—	0.04	—	1551,1566	—	rd	—
VW 1.0%	1.89	—	1.29	—	0.13	—	0.09	—	1551, 1566	—	rd	—
VW 5.0%	—	3.68	—	1.75	—	0.29	—	0.12	—	1551, 1566	—	rd
VWS 1.0%	*0.38*	1.18	*0.22*	0.59	—	0.12	—	0.06	—	—	nrd	rd
VWS 5.0%	1.36	—	1.16	—	0.10	—	0.06	—	1551, 1566	—	rd	—
VFG 1.0%	*0.43*	—	*0.18*	—	—	—	—	—	—	—	nrd	—
VFGP 1.0%	*0.36*	*0.35*	*0.29*	*0.20*	—	—	—	—	—	—	nrd	nrd
VRG 1.0%	*0.43*	*0.40*	*0.24*	*0.19*	—	—	—	—	—	—	nrd	nrd
Painting	*0.36*	*0.45*	*0.20*	*0.17*	—	—	—	—	—	—	—	—
Vulpex	16.81		10.79		1.01		0.65		1551, 1566	—	—	

potential for the treatment of small areas or of surfaces that are vulnerable to mechanical action (Table 2). The amount of potassium found on the surface (SEM-EDS) and the increase in the pH values coincide with the results obtained by means of GC-MS and FTIR, which highlighted the presence of Vulpex in the painting (Table 3).

TABLE 3. Amount of potassium detected by scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS) and pH values on the treated surfaces. A dash (—) indicates that no measurements were made. V = Vulpex; W = water; WS = white spirit; FG = fluid gel; FGP = fluid gel applied on barrier paper; RG = rigid gel.

Cleaning system	K ion detected weight for P1 (%)	pH	
		P1	P2
VW 0.5%	3.8	8.4	—
VW 1.0%	4.7	9.5	—
VW 5.0%	—	—	9.4
VWS 1.0%	0.72	6.8	6.5
VWS 5.0%	6.6	9.6	—
VFG 1.0%	0.53	6.7	—
VFGP 1.0%	0.42	6.8	6.5
VRG 1.0%	0.56	6.8	6.4
Untreated painting	0.56	6.7	6.4

Assessment of Alterations on the Paintings: Analysis of Swab Extracts

The assessment of painting surface damage from cleaning processes based on experimental models is a complex issue: it is difficult to extrapolate the results to real works because of the large number of factors that affect deterioration processes. Phenix and Sutherland (2001) focused on this problem in an article on the effects of organic solvents on oil paint layers and included a description of the advantages and drawbacks of some experimental designs. Several studies carried out on paintings manufactured in laboratories and the immersion of samples in different solvents served to improve our understanding, in a controlled environment, of many of the processes and risks involved in painting deterioration (Sutherland, 2003, 2006).

Several premises that have led us to the application of cleaning protocols similar to those used in restoration have been taken into account for the qualitative evaluation of surface damage in samples treated with the different cleaning systems. First, half the treatments used in this study were not applied in liquid form, but were gelled, and furthermore, previous publications that describe the potential damage from Vulpex solutions with high soap concentrations were taken into consideration. Second, the painting in the test samples and the painting selected for the restoration team were different, so there were fewer variables that could have a bearing on the differences or similarities in the results if the same cleaning and rinsing procedures were applied.

One of the markers that points toward particle dragging with the rinsing swab is the existence of azelaic acid as well as

palmitic and stearic acids since azelaic acid is only found in the oil of a dry paint film. This method can only be used to perform a qualitative estimate of the paint dragging process and does not explain the factors behind the damage and the way in which it may have occurred. Furthermore, the semiquantitative calculation of the fatty acids that had been dragged with the cotton swab may help us estimate the vulnerability of the studied surfaces to the different cleaning treatments.

In general, the amount of azelaic acid found in the swabs from the two paintings was low, especially in areas treated with Vulpex in an aqueous solution or in fluid gel. The painting treated by the restoration team showed the greatest amount of azelaic acid extracted in the swabs, specifically in the area that was cleaned with the solution with the highest concentration (5%) (Figure 3).

It is important to note that in the case of the test samples treated only with water the number of times the moist swab was run over the surface was equivalent to the soap application and the rinsing. No azelaic or stearic acids were found on the swab in this case, and the amount of palmitic acid was the lowest. This means that the negative effect on the painting surface stems from the soap in the aqueous medium, regardless of its application method.

No azelaic acid was found on the test samples where soap in white spirit was used in any concentrations. However, varying amounts of dicarboxylic acid were detected in the swabs used for the older painting (P2), especially in a dark area with umber pigments.

The barrier paper used in test samples treated with gelled systems did not prevent paint particle dragging, although the extent of particle detachment was lower than in the areas where gel was applied directly on the painting. Similarly, the barrier paper did not prevent fatty acids from being found on the cleaning swab from the painting treated by the restoration team. Here the swabs showed the highest value of palmitic acid, possibly because the painting was older and its free fatty acid content was greater, although it is also true that the rinsed area was larger. The cleaning treatments with rigid gels were not rinsed with swabs; therefore, they are not included in Figure 4, where the results of the fatty acid measurements are summarized.

Observed Damages on the Paintings after Cleaning Treatments

Damage evaluation by means of SEM and CSM was only performed on the P1 test samples. In these cases, controls with water and with a rigid agar gel without Vulpex were applied to check the effect these elements had on the painting.

SEM

Several research papers applied scanning electron microscopy to evaluate changes in the painted surfaces after cleaning (Burnstock and White, 1990; Hedley et al, 1990; Morrison et al., 2007). In this study, images at 30× and 100× were used to evaluate the changes caused by the different treatments. Images at 500× revealed small particles and the texture of the painted surfaces. The main types of damage observed were cracking,

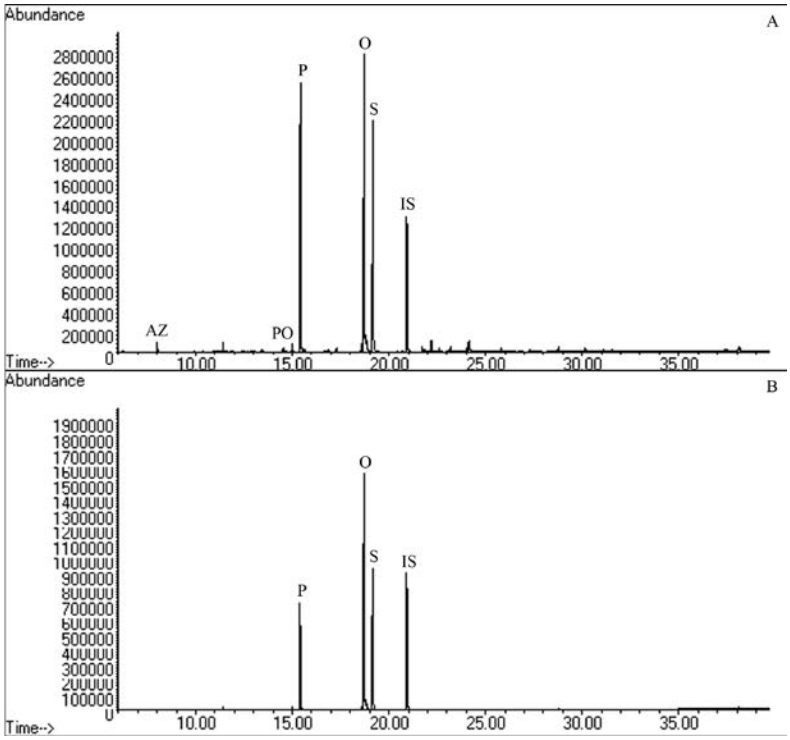


FIGURE 3. Chromatograms of the extracts from the rinsing swabs from treatments of painting P2 with (A) VW 5.0% and (B) VWS 5.0%. The top chromatogram shows dimethyl azelate (AZ), which means that paint dragging has occurred. The bottom chromatogram shows methyl palmitate (P), methyl stearate (S), and a large amount of methyl oleate (O) from the Vulpex. IS corresponds to the internal standard, methyl nonadecanoate.

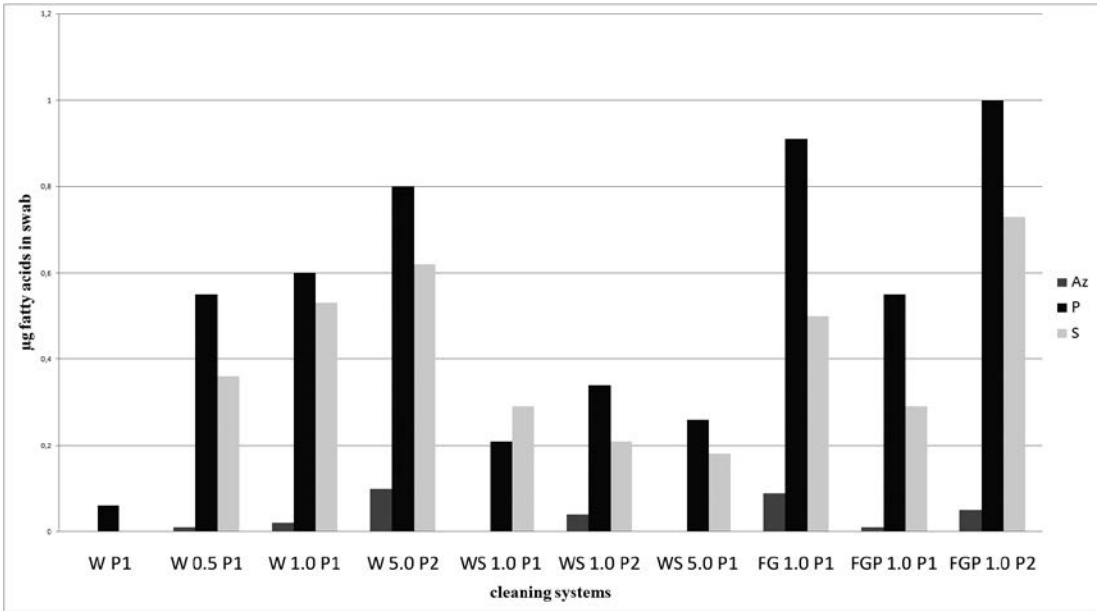


FIGURE 4. Fatty acids measured in the rinsing swabs used in paintings P1 and P2 after the treatments with water (W), soap in water (W0.5, W1.0, W5.0), soap in white spirit (WS1.0, WS5.0), fluid gels (FG1.0), and fluid gel applied on barrier paper (FGP1.0).

flattening of the surface and detachment or removal of paint particles (Figure 5).

In general, thin cracks were seen to become larger whenever aqueous or gelled solutions were applied. Apart from this, rigid gels (both clear gels and gels containing Vulpex) also caused small fissures. No surface cracks were found in test samples treated with the solutions of soap in white spirit. Flattening of the paint was evident in the treatments with aqueous soap solutions, in paintings that were cleaned with fluid gel, especially the one where Japanese paper was used, and in those treated with rigid gels. Particle detachment or material removal was clearly seen in test samples treated with fluid gels that were applied following both methods in the test.

CSM

One of the most common methods used in industry to quantify the roughness of a surface is based on recording height profiles by means of a roughness meter or profilometer. Data are treated statistically to determine parameters such as the average roughness R_a, and they provide useful information on the quality of different processes, even if they cannot be considered properties of surfaces (Hinojosa and Reyes, 2001).

Variations in the roughness profiles have been used in operations with cultural objects, especially to monitor changes after applying various cleaning systems (Blanco et al., 2008; van den Berg et al., 2008). Atomic force microscopy has also been useful for pinpointing topographical variations in paintings treated with different cleaning systems (Ormsby et al., 2006). The ability to measure the depth of the cracks and to obtain images with false coloring that illustrates other modifications, such as detachment and dragging of particles, is an important confirmation and complement to the SEM observations. The results of the modifications in the P1 test samples are presented in Table 4.

The surface that was treated with water showed a slight increase in roughness because of the softening of the surface and the movement of particles, which led to an irregular topography. Aqueous soap solutions (VW 0.5% and VW 1.0%) caused flattening of the surface, and this was related to a decrease in roughness. In these cases, paint particles were removed in a medium that was already softer because of the water. The effect was increased with a greater soap concentration.

The solutions of Vulpex in white spirit (VWS 5.0%) showed little roughness variations. This treatment only showed slight movement of particles on the paint surface. However, no damage was found on surfaces treated with a solution of 1% of soap in white spirit.

The roughness variation values were different in the test samples treated with fluid gels directly on the painting or on the barrier paper. In the former case (VFG 1.0%), the roughness increased because of particle detachment and accumulation and the appearance of cracks of up to 15 μm in depth. In the latter case (VFGP 1.0%), roughness values decreased by more than 5% with the barrier paper because the surface became flatter and particles were dragged in the rinsing swab, as verified in the GC-MS analyses. Deep cracks were also found in this case,

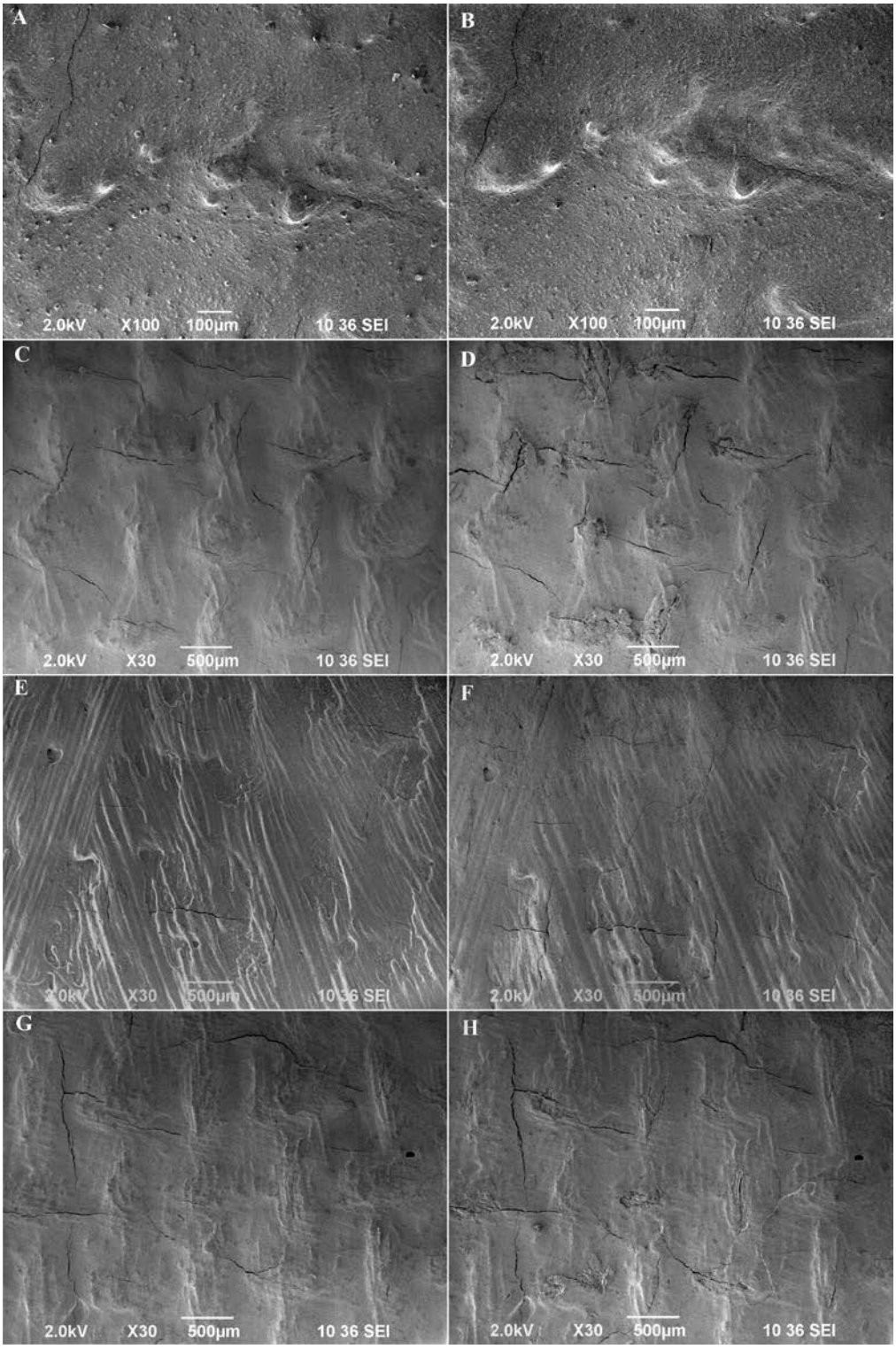


FIGURE 5. Scanning electron microscopy images with examples of the damage observed on the painting surface. The images were taken (left) before and (right) after the cleaning. B (VWS 1.0%) does not present significant surface changes, D (VFGP 1.0%) shows increased cracking, F (VRG 1.0%) shows surface flattening, and H (VFG 1.0%) shows particle dragging and removal.

TABLE 4. Roughness variation as measured by CSM and main damage observed on the painting surfaces. Roughness variation is the average value of measurements taken in 10 areas 1.46 × 1.10 mm^2 in size. W = water; V = Vulpex; WS = white spirit; FG = fluid gel; FGP = fluid gel applied on barrier paper; RG = rigid gel.

	General roughness variations	
Treatments	Roughness variation (%)	Main damage
W	0.60	Movement of particles
VW 0.5%	–1.46	Flattening of the surfaces and particle removal
VW 1.0%	–1.81	Flattening of the surfaces and particle removal
VWS 1.0%	0.30	Slight particle movement
VWS 5.0%	0.33	Slight particle movement
VFG 1.0%	2.46	Particle detachment and accumulation and appearance of deep cracks
VFGP 1.0%	–5.22	Flattening of the surfaces, particle dragging, and appearance of deep cracks
RG	–1.87	Flattening of the surfaces and appearance of thin cracks
VRG 1%	1.05	Flattening of the surfaces and appearance of deep cracks

although they were fewer in number than with the previous system (Figure 6).

The cleaning with clear agar gel (RG) showed surface flattening that was caused by the joint action of two factors. First, the water softened the paint, and second, the slight pressure applied to keep the gel in contact with the paint caused a reduction in the roughness. In this case, only thin cracks were found. Adding Vulpex to the rigid gel (VRG 1.0%) would produce an increase in the roughness because soap causes deeper cracks to open.

CONCLUSIONS

The methodology used in this study served to evaluate the residues of the Vulpex commercial soap on the surface of paintings after cleaning. The study showed mainly qualitative differences between the various cleaning treatments.

The results suggest that Vulpex is not appropriate to eliminate dirt in young unvarnished paintings because of the deterioration induced by this product on the paintings, as had already been highlighted in other studies with different paintings and at different concentrations. All the surfaces treated with aqueous solutions of Vulpex had residues after the cleaning except when treated with a 1% soap solution in white spirit; the application was carried out at this same concentration in water but was applied as fluid or rigid gel, or the fluid gel was applied with a barrier paper.

In general, all the paintings treated with Vulpex in this study showed surface damage. This was linked to the effect of the soap, the application method, and the rinsing processes. The main damage observed was cracking, surface flattening, and paint particle removal. Rigid gel systems were the least damaging, and they seemed to be more practical for local treatments.

A good correlation was found between the results of the P1 test samples and those obtained with the painting cleaned by the professional restoration team (P2). Furthermore, the results from the restorers did not present important variations. Instead, variations seemed to stem from the area of the painting on which the treatment was applied. The inclusion of the results of these studies in the technical files of companies specializing in restoration product distribution is a positive measure to reduce risks related to the use of commercial soaps.

Acknowledgments

The authors thank Luis Alberto Angurel at the Instituto de Ciencia de Materiales y Fluidos, Universidad de Zaragoza, for his contribution to the CSM studies; restorers Raquel Sáez, Susana Pérez, Alejandra Martos, Juan Alberto Soler, Marta Palau, and Susana Lozano for assisting with the cleaning treatments carried out in conjunction with the experiments; the distributors specializing in restoration products, Agar-Agar SL, C.T.S. España Productos y Equipos para la Restauración S.L., Productos de Conservación SA, and STEM Servicios Técnicos y Equipamiento para Museos; and, in particular, Ubaldo Sedano, Jorge García, and Pilar Sedano, the heads of the restoration departments at the Museo Thyssen Bornemisza, Museo Nacional Reina Sofía, and Museo Nacional de Prado, respectively, for supporting this project.

APPENDIX A: INSTRUMENTAL OPERATION CONDITIONS

GC-MS. An Agilent Technologies GC-6890N–MS 5973 chromatograph, with a HP-5MS (5% phenyl, 95% dimethylpolysiloxane) capillary column (length: 30 m, internal diameter: 250 μm × film thickness: 0.25 μm) and with a flow of 1 mL/min of helium as the carrier gas, was used. The oven

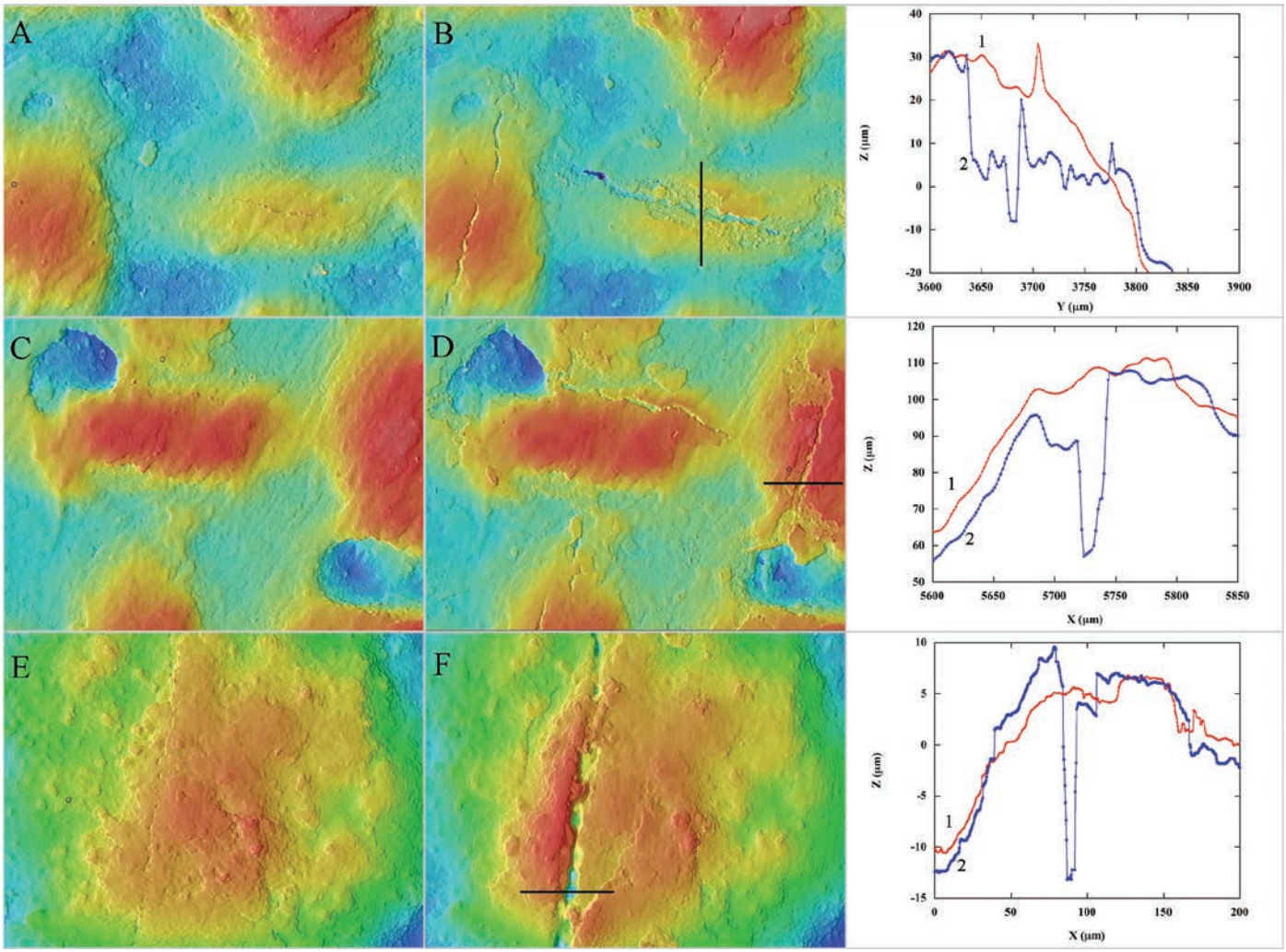


FIGURE 6. Confocal scanning microscopy images with examples of the damage on the surface of painting P1 (left) before and (middle) after cleaning with VFGP 1.0%. (right) The surface roughness plots are shown for before (red line, labeled 1) and after (blue line, labeled 2) cleaning along the lines marked in black on the cleaned images. It can be seen that the cracking and particle dragging have changed the area roughness, as shown in the corresponding graphs (A and B). The central image shows a deep crack and particle dragging in other areas of the section displayed (C and D). E and F show a deep crack that developed after the treatment. The size of this crack is greater than 15 μm, as shown in the graph on the right.

was programmed to start at 100°C, held there for 0.5 minute, increased by 40°C/min to 150°C, held there for 3.0 minutes, then increased by 5°C/min to 300°C, and held there for 5 minutes. The ionization mode was an electron impact (EI^+) m/z range between 50 and 550. The data were acquired and processed with the ChemStation Agilent program.

FTIR-ATR. A Nicolet 6700 spectrometer and an attached Smart Orbit Diamond 30,000–200 cm^{-1} ATR (attenuated total reflectance) accessory were used. The spectra were recorded between 4,000 and 500 cm^{-1}.

SEM-EDS. The optimum conditions for the surface imaging were as follows: acceleration voltage = 2 kV, aperture setting = 2, spot size = 36, and *z* coordinate = 10 mm. Elemental microanalysis was performed by an Oxford Instruments INCA X-ray microanalysis system.

APPENDIX B: MATERIALS AND SUPPLIERS

Vulpex: Productos de Conservación SA
Methanol: Fluka, product number 65554-1L
White spirit (~17% aromatic): Fluka, product number 864660
Agar: Fluka, product number 05040

MethPrep II (m-(trifluromehyl) phenyltrimethylammonium hydroxide, 0.2 N in methanol): Alltech, product number (800) 255-8324

KBr: Panreac, product number 331489.1609

Klucel G: CTS ESPAÑA productos y equipos para la Restauración S.L.

Japanese paper: Sekishu Thin 13.5g/m^2: Arte & Memoria SL, product number 200628

REFERENCES

Anzani, M., M. Berzioli, M. Cagna, E. Campani, A. Casoli, P. Cremonesi, M. Fratelli, A. Rabbolini, and D. Riggardi. 2008. *Use of Rigid Agar Gels for Cleaning Plaster Objects*. Quaderni CESMAR7, No. 6. Padua: Il prato.

Blanco, M., O. Buj, and M. F. Colucci. 2008. Caracterización de Tratamientos de Limpieza Mediante Microscopía Confocal. [Characterization of Cleaning Treatments by Conformal Microscopy.] *Macla,* 9:57–58.

Bueno, J. M., J. Modenés, and J. Bueno. 2004. "Los problemas de los disolventes clásicos en limpieza de pintura al óleo: Soluciones con los de nueva generación." [Problems of Classic Solvents in the Cleaning of Oil Paintings: Alternatives with New Generation Solvents.] In *Proceedings of the 15th Congress Conservación y Restauración de Bienes Culturales*, pp. 213–220. Murcia, Spain: Consejería de Educación y Cultura, Dirección General de Cultura.

Burnstock, A., and R. White. 1990. "The Effects of Selected Solvents and Soaps on a Simulated Canvas Painting." In *Cleaning, Retouching and Coatings: Preprints of the IIC Brussels Congress*, ed. J. S. Mills and P. Smith, pp. 111–118. London: International Institute for Conservation.

Carlyle, L., J. H. Townsed, and S. Hackney. 1990. "Triammonium Citrate: An Investigation into Its Application for Surface Cleaning." In *Dirt and Picture*, ed. V. Todd, pp. 44–48. London: United Kingdom Institute of Conservation.

Campani, E., A. Casoli, P. Cremonesi, I. Saccani and E. Signorini. 2007. *Use of Agarose and Agar for Preparing "Rigid Gels."* Quaderni CESMAR7, No. 4. Padua: Il prato.

Conservation by Design. 2005. Technical Data Sheet: Vulpex Liquid Soap (SR7). http://www.conservation-by-design.co.uk/pdf/datasheets/Vulpex Liquid Soap SR7- data sheet.pdf (accessed 26 November 2012).

Cremonesi, P. 2004. "Gli addensanti e i supportanti." [Thickening and Supporting Agents]. In *L'uso dei solventi organic nella pulitura di opere policrome* [The Use of Organic Solvents in the Cleaning of Polychromed Works], pp. 45–51. Padua: Il prato.

Cremonesi, P., and L. Borgioli. 2008. Notes from the Technical Meeting "Disolventes, soluciones acuosas y nuevos polímeros para la restauración." [Solvents, Aqueous Solutions and New Polymers for Restoration.] Madrid: Museo Nacional Centro de Arte Reina Sofía. http://ge-iic.com/index.php?option=com_content&task=view&id=307&Itemid=37 (accessed 26 November 2012).

Hedley, G., M. Odlyha, A. Burnstock, J. Tillinghast, and C. Husband. 1990. "A Study of Mechanical and Surface Properties of Oil Paint Films Treated with Organic Solvents and Water." In *Cleaning, Retouching and Coatings*: *Preprints of the IIC Brussels Congress,* ed. J. S. Mills and P. Smith, pp. 98–105. London: International Institute for Conservation.

Hinojosa, M., and M. E. Reyes. 2001. La rugosidad de las superficies: Topometría. [Surface Roughness: Topometry.] *Ingenierías*, 4(11):27–33.

Morrison, R., A. Bagley-Young, A. Burnstock, K. J. van den Berg, and H. van Keulen. 2007. An Investigation of Parameters for the Use of Citrate Solutions for Surface Cleaning Unvarnished Paintings. *Studies in Conservation,* 52(4): 255–270.

Ormsby, B., T. Learner, M. Schilling, J. Druzik, H. Khanjian, D. Carson, G. Foster, and M. Sloan. 2006. The Effects of Surface Cleaning on Acrylic Emulsion Paintings: A Preliminary Investigation. *Tate Papers*, 6. http://www.tate.org.uk/research/publications/tate-papers/effects-surface-cleaning-on-acrylic-emulsion-paintings-preliminary (accessed 26 November 2012).

Osete-Cortina, L., and M. T. Doménech-Carbó. 2005. Study on the Effects of Chemical Cleaning on Pinaceae Resin-Based Varnishes from Panel and Canvas Paintings Using Pyrolysis-Gas Chromatography/Mass Spectrometry. *Journal of Analytical and Applied Pyrolysis*, 76:144–153.

Phenix, A., and K. Sutherland. 2001. The Cleaning of Paintings: Effects of Organic Solvents on Oil Paint Films. *Reviews in Conservation*, 2:47–60

Ross, S., and A. Phenix. 2005. Vulpex™ Spirit Soap as a Cleaning Agent for Painted Surfaces. *WAAC Newsletter,* 27(1):15–22.

Sánchez-Ledesma, A., I. González, M. del Mazo, A. Muñoz, L. Tormo , and A. Jorge. In press. "Estudio mediante SEM y CSM de escayolas tratadas con geles rígidos y aditivos." [SEM and CSM Study of Plasters Treated with Rigid Gel and Additives]. In *Proceedings of 11th Meeting Conservación de Arte Contemporáneo*. Madrid: Museo Nacional Centro de Arte Reina Sofía.

Sánchez-Ledesma, A., C. Muro, and M. D. Gayo. 2008a. "Determinación de residuos del jabón comercial Vulpex empleado en la limpieza de superficies pintadas jóvenes sin barnizar." [Residue Detection of Commercial Vulpex Soap Used for the Cleaning of Recent Unvarnished Paintings.] In *Proceedings 9th Meeting Conservación de Arte Contemporáneo,* pp. 71–81. Madrid: Museo Nacional Centro de Arte Reina Sofía.

———. 2009. "Evaluación de los residuos de dos jabones comerciales aplicados sobre superficies jóvenes pintadas no barnizadas: Vulpex en disolvente orgánico y Contrad 2000." [Residue Evaluation Left on Recent Unvarnished Paintings by Commerial Soaps: Vulpex and Contrad 2000.] In *Proceedings 10th Meeting Conservación de Arte Contemporáneo,* pp. 125–133. Madrid: Museo Nacional Centro de Arte Reina Sofía.

Sánchez-Ledesma, A., U. Sedano, A. Martos, S. Pérez, and J. A. Soler. 2008b. "Detección de residuos en superficies barnizadas tratadas con jabón de resina aplicado sobre diferentes papeles de barrera." [Identification of Residues from Varnished Surfaces after Treatment with Resin Soaps Applied over Different Barrier Papers.] Technical report. Madrid: Museo Thyssen–Bornemisza.

Southall, A. 1990. "Detergents Soaps Surfactants." In *Dirt and Picture*, ed. V. Todd, pp. 29–34. London: United Kingdom Institute of Conservation.

Stulik, D., D. Miller, H. Khanjian, N. Khandekar, R. Wolbers, J. Carlson, and W. C. Petersen. 2004. *Solvent Gel for the Cleaning of Works of Art: The Residue Question*. Edited by V. Dorge. Los Angeles: The Getty Conservation Institute.

Sutherland, K. 2003. Solvent-Extractable Components of Linseed Oil Paint Films. *Studies in Conservation*, 48(2):111–135.

———. 2006. Measurements of Solvent Cleaning Effects on Oil Paintings. *Journal of the American Institute for Conservation*, 45(3):211–226.

van den Berg, K. J., M. Daudin, I. Joosten, B. Wei, R. Morrison, and A. Burnstock. 2008. "A Comparison of Light Microscopy Techniques with Scanning Electron Microscopy for Imaging the Surfaces Cleaning of Paintings." Paper presented at 9th International Conference on NDT of Art, Jerusalem. http://www.ndt.net/article/art2008/papers/033VandenBerg.pdf (accessed 18 May 2010).

Wolbers, R. 2000. *Cleaning Painted Surfaces: Aqueous Methods*. London: Archetype Publications.

Extended Abstract—Tissue Gel Composite Cleaning

Gwendoline Fife, Jos Van Och, Kate Seymour, and Rene Hoppenbrouwers

INTRODUCTION

In the recent past, the Stichting Restauratie Atelier Limburg (SRAL) developed a method for removing varnish from the surface of paintings by employing tissues saturated with simple solvent gels (comprising organic solvent and cellulose ether gelling agents only). Initially conceived for treating paintings in the Oranjezaal, Huis ten Bosch, the Netherlands (Van Och et al., 1999), the use of solvents gelled and applied in this manner proved to have several advantages over their use as free solvents. The technique outlined here, with adaptations to the individual requirements of the painting, has since been employed in a variety of projects at SRAL. A fuller description of this technique can be found elsewhere (Fife et al., 2011).

TECHNIQUE DESCRIPTION

A fundamental aspect of the technique is the application of a special tissue (synthetic nonwoven untreated cleaning cloth; see the Appendix) saturated with a cellulose ether-gelled solvent. After a solvent (or solvent mixture) is selected, it is thickened to a gel state by gradually adding a cellulose ether under rapid mixing conditions, initially using a mechanical or handheld whisk, followed by magnetic stirring in proportions varying from 2% to 4% (by weight of cellulose ether to volume of solvent) depending on the viscosity of the gel required in the particular situation. When a uniform gel is achieved, it is then brush applied to each individual tissue. This composite is applied to the varnished painting surface and left for a period of time (pre-ascertained by testing but generally no longer than 60 seconds) until the non-original coatings have been dissolved (Figure 1). A dry absorbent tissue is then placed on top, and the mixture of (still wet) gel and dissolved varnish residues is then gently pressed into this upper tissue. Both tissues are then simultaneously peeled back from the painting, revealing the cleaned painting surface. This system can also be effective in concurrently removing varnish, non-original overpaints, and retouches.

The known practical advantages over free solvent cleaning are the following:

- The system is more efficient since every moment that the solvent (in gelled form) is in contact with the surface it is being "used" (as opposed to swab with free solvent cleaning).

Gwendoline Fife, Jos Van Och, Kate Seymour, *and* ***Rene Hoppenbrouwers****, Stichting Restauratie Atelier Limburg, Avenue Céramique 224, 6221 kx Maastricht, PO1679, Maastricht 6201BR, the Netherlands. Correspondence: Gwendoline Fife, retrae@sral.nl; gwenfife26@hotmail.com.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

FIGURE 1. Varnished painting surface is still visible through gel-saturated tissue.

- A very even level of varnish removal can be achieved that conforms to the surface topography.
- The technique prevents solvent and dissolved varnish residues traveling through cracks to the reverse of the painting, a factor considered particularly advantageous in the cleaning of both unlined and previously uncleaned paintings.
- Residues of varnish, old overpaints, and other non-original material already present within the cracks in the paint layer are dissolved and removed without being smeared and redeposited across the painting surface (Figure 2).
- With the enclosed-pack system, the gelled tissues can be prepared in advance under good extraction conditions in multiple units. This ensures greater uniformity in gel distribution between tissues and a reduction in both the conservator's exposure to solvent and the time required for the tissue preparation.

Further advantages to be considered are the following:

- The gel-tissue technique prevents solvent movement (by capillary action) through the painting structure, thus avoiding the creation of new swelling fronts within the paint structure.

FIGURE 2. Simultaneous removal of varnish and old overpaints (including nonoriginal material already present within the cracks in the paint layer).

- The capillary action of the tissue encourages the diffusing solvent to evaporate back out toward the front of the painting (rather than farther into the paint film).
- A lower mechanical action is imposed on the paint film.

However, the following problematic issues remain:

- Although the only nonvolatile components of these gels are the more stable cellulose ethers, it is still undesirable that any residues be left on the painting surface.
- Because of the choice of these gelling agents, the solvent selection for the current SRAL system is limited.

CONCLUSION

The technique described has demonstrated some general advantages over using swabs with free solvent that has rendered it more appropriate to use for certain cleaning problems. However, improvements are still desired and anticipated. Hence, investigations into other simple and stable gelling agents and alternative matrix systems for solvent containment are continuing. Furthermore, an evaluation of this cleaning system with regard to its effect on the diffusion of solvents into the original materials (with the associated risk of swelling and leaching of mobile components from within the paint film) is planned.

APPENDIX

Suppliers of tissues currently used at SRAL are as follows. Tissue for gel impregnation is schoonmaakdoek RR, 33 × 40 cm , article 2516, manufactured by Hanotex International BV, Joure, the Netherlands (http://www.hanotex.nl). The absorbing tissue is Kimtech 7506 dry absorbent towels, manufactured by Kimberly-Clark Professional (http://www.kimberly-clark.com).

REFERENCES

Feller, R. L., and M. Wilt. 1990. *Evaluation of Cellulose Ethers for Conservation*. Los Angeles: The J. Paul Getty Trust.

Fife, G. R., J. van Och, B. Stabik, N. Miedema, K. Seymour, and R. Hoppenbrouwers. 2011. "A Package Deal: The Development of Tissue Gel Composite Cleaning at SRAL." In *ICOM-CC Lisbon 2011 Abstracts, 16th Triennial Conference, Lisbon,19–23 September 2011,* ed. J. Bridgland, p. 172. Almada, Portugal: Critério.

Van Och, J., J. Shepard, L. Speleers, D. Schellaars, and J. Van Der Werf. 1999. Condition and Treatment Report for Jacob Jordaens '*Prince Frederik Hendrik van Oranje als Triomfator.*' Internal report, Oranjezaal Project, Huis Ten Bosch (1997–2001). Maastricht, the Netherlands: Stichting Restauratie Atelier Limburg.

Extended Abstract—Partially Hydrolyzed Polyvinyl Acetate and Borax Gels for Cleaning Painted Surfaces

Lora V. Angelova, Barbara H. Berrie, and Richard G. Weiss

INTRODUCTION

A variety of water-based gels have been used for cleaning works of art, but many of them have undesirable properties. Gel-like materials (hereafter referred to as gels) based on polyvinyl alcohol have been investigated in an effort to expand the range of options for conservators. Polyvinyl alcohol can be cross-linked with borax to form well-characterized hydrogels (Sinton, 1987). Previous studies have shown that no more than 30% of the gelated liquid can be composed of an organic solvent (Carretti et al., 2009). The present study reports that polyvinyl acetate (PVAc) with reduced hydrolysis fractions can form borax cross-linked gels with a large mole fraction of methanol, ethanol, 1- and 2-propanol, acetone, or *N*-methyl pyrrolidinone (NMP) as a cosolvent with water (Angelova et al., 2011; Natali et al., 2011). The gels can be made nonsticky, transparent, pliant, and stable over periods of at least weeks in closed vessels at room temperature (Figure 1). As such, they show great potential for the removal of dirt and other coatings from sensitive and delicate surfaces.

PVAC GELS

The properties of these gels prepared from several samples of polyvinyl acetate with varying degrees of hydrolysis (40%, 45%, 75%, and 80%; henceforth, 40-PVAc, 45-PVAc, etc.) and a wide range of molecular weights are being investigated. The amount of organic solvent that can be incorporated into the gels is strongly dependent on the hydrolysis degree of the polyvinyl acetate. Gels with up to 80% of polar, organic solvents can be formed from 40-, 45-, and 75-PVAc. When the hydrolysis degree is increased to 80%, gels are stable only up to a 1:1 mixture of water and organic solvent. When preparing gels from the low hydrolysis grade polymers (40-, 45-, and 75-PVAc), 20% of the solvent mixture is the water necessary for dissolving the borax. The measured pH of many of these gels is between 8 and 9, although these values are difficult to measure in the presence of large quantities of alcohols. The polymer weight fractions used to prepare the gels depend on the molecular weight of the polyvinyl acetates as well as the amount of residual acetate monomers present.

It has been found that the most thermally stable gels are formed when the hydroxyl monomer to borate ion ratio is about 15:1 as determined by the falling drop method

Lora V. Angelova *and* ***Richard G. Weiss****, Chemistry Department, Georgetown University, Washington, DC 20057, USA.* ***Barbara H. Berrie****, National Gallery of Art, Washington, DC 20565, USA. Correspondence: Lora V. Angelova, lva2@georgetown.edu; Richard G. Weiss, weissr@georgetown.edu; Barbara H. Berrie, b-berrie@nga.gov.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

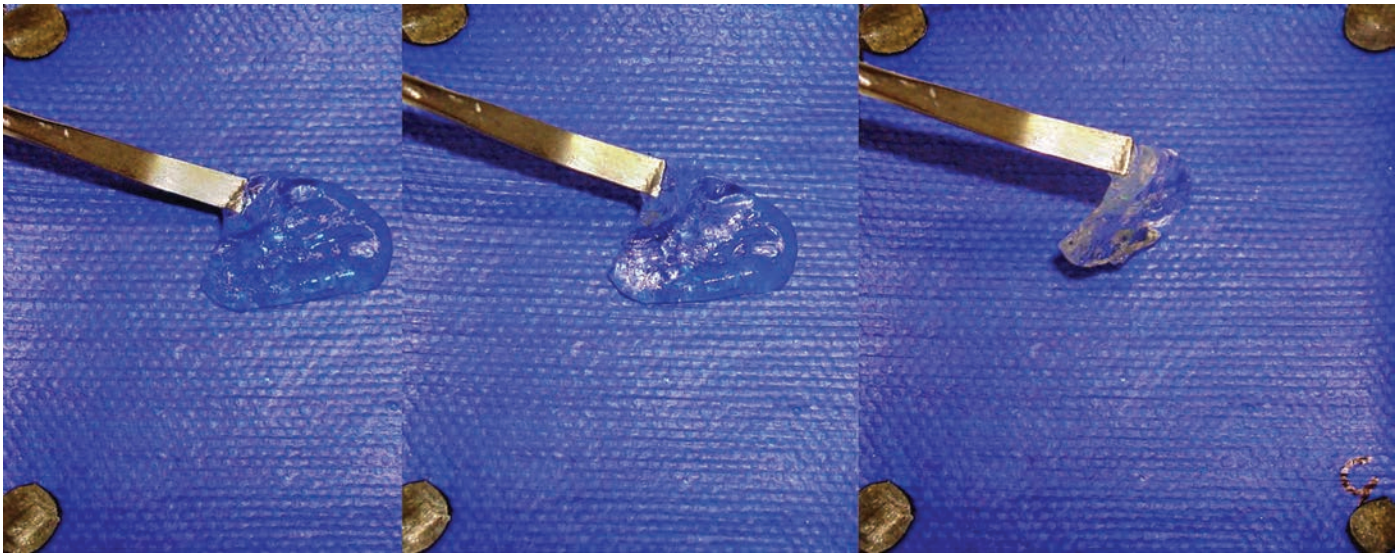


FIGURE 1. A gel, composed of 6% w/v 75-PVAc and 1.4% w/v borax with a 50:50 ethanol:water solvent composition, being removed from an acrylic test surface.

(Raghavan, and Cipriano , 2005). Although these gels are stable and can resist flow at increased temperatures (sometimes as high as 100°C), they are also very hard and brittle (as opposed to the typical hydrogel putty-like texture). It was also noted that increasing the organic content in the gels makes them stiffer. Melting range tests on gels prepared from the different polymer samples and with varying ratios of water to organic solvents (methanol, ethanol, 1-propanol, and NMP) show similar trends: increasing organic content results in higher thermal stability. A gel prepared from 75-PVAc (6% w/v) and borax (1.4% w/v) begins to flow at 45°C when 10% v/v of the gelated solvent is methanol. When the methanol content is increased to 70% v/v, the gel does not flow until a temperature of 75°C is reached (Angelova et al., 2011).

The pliability of the gels can be controlled by reducing the weight fraction of borax in the system. When the organic content is high (80% v/v of ethanol or 1-propanol) and the borax concentration is reduced gradually from 2% to 0.3% w/v, a dramatic difference is observed in the handling properties of the gels. Those gels with intermediate amounts of cross-linking agent (0.7%–1.0% w/v) can easily be pressed between two sheets of Mylar into a thin membrane that can then be placed onto the surface to be cleaned. Such gels prepared from 45-PVAc (11% w/v) with 80% v/v 1-propanol and varying amounts of borax have been tested on acrylic surfaces. Gels with a very low borax concentration (0.3%–0.5% w/v) tend to be more difficult to remove, leave some visible gel residue, and lose solvent faster. Increased concentrations of cross-linking result in reduced solvent evaporation and increased ease of removal. No visible gel residue was left on an acrylic test surface after a five-minute treatment with these formulations.

Fluorescein has been incorporated into the gelated solvent and covalently attached to the polymer chains (Guan et al., 2006). Fluorescent gels are being used to monitor solvent loss from the gel, both peripherally and into the surface layers. Using excitation-emission spectroscopy, gels prepared from fluorescein-derivatized polymers have been shown to leave no deposit on an acrylic test panel (Figure 2).

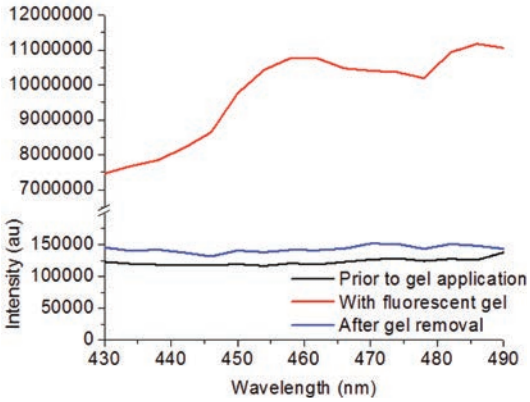


FIGURE 2. Excitation spectra of a canvas surface with a layer of acrylic paint before (black) and after application (red) and after removal (blue) of a gel composed of 6% w/v 75-PVAc with covalently bound fluorescein, 1.4% w/v borax, and a 30:70 methanol:water solvent. Please note that there is no significant difference in the spectra of the initial state (black) and the final state (blue) after removal of the gel.

Thus far, gels with 80% ethanol and 20% water have been used to remove the top layer of unbleached shellac from a nineteenth-century Italian wooden frame with a gesso underlayer as a base to a yellow bole for the silver leaf. Complete removal of the shellac was confirmed by fluorescence analysis. Similarly, application of these gels to acrylic paint test surfaces has been attempted. It appears that gels containing large amounts of water may be particularly suitable for this purpose. Currently, new polymers are being designed that will help expand the list of gelated solvents.

Acknowledgments

The Georgetown authors gratefully acknowledge the U.S. National Science Foundation for its support of this research. The authors also thank Jay Krueger and Kristin deGhetaldi for helpful discussions.

REFERENCES

Angelova, L. V., I. Natali, E. Carretti, P. Terech, L. Dei, and R. G. Weiss. 2011. Cosolvent Gel-like Materials from Partially Hydrolyzed Poly(vinyl acetate) s and Borax. *Langmuir*, 27(18):11,671–11,682. http://dx.doi.org/10.1021/la202179e.

Carretti, E., S. Grassi, M. Cossalter, I. Natali, G. Caminati, R. G. Weiss, P. Baglioni, and L Dei. 2009. Poly(vinyl alcohol)-Borate Hydro/Cosolvent Gels: Viscoelastic Properties, Solubilizing Power, and Application to Art Conservation. *Langmuir*, 25(15):8656–8662. http://dx.doi.org/10.1021/la804306w.

Guan, X., X. Liu, Z. Su, and P. Liu. 2006. The Preparation and Photophysical Behaviors of Temperature/pH-Sensitive Polymer Materials Bearing Fluorescein. *Reactive and Functional Polymers*, 66:1227–1239. http://dx.doi.org/10.1016/j.reactfunctpolym.2006.03.005.

Natali, I., E. Carretti, L. V. Angelova, P. Baglioni, R. G. Weiss, and L. Dei. 2011. Structural and Mechanical Properties of "Peelable" Organoaqueous Dispersions with Partially Hydrolyzed Poly(vinyl acetate)-Borate Networks: Applications to Cleaning Painted Surfaces. *Langmuir*, 27(21):13,226–13,235. http://dx.doi.org/10.1021/la203452e.

Raghavan, S. R., and B. H. Cipriano. 2005. Gel Formation: Phase Diagrams Using Tabletop Rheology and Calorimetry. In *Molecular Gels: Materials with Self-Assembling Fibrillar Networks,* ed. R. G. Weiss and P. Terech, pp. 243–245. Dordrecht, Netherlands: Springer.

Sinton, S. W. 1987. Complexation Chemistry of Sodium Borate with Poly(vinyl alcohol) and Small Diols. A ^{11}B NMR Study. *Macromolecules*, 20:2430–2441. http://dx.doi.org/10.1021/ma00176a018.

Extended Abstract—Use of Agar Cyclododecane for Cleaning Tests on a Frail Painting

Alberto Finozzi, Alessandra Sella, and Chiara Stefani

INTRODUCTION

The painting representing the Battle of San Martino (24 June 1859), also known as the battle of Solferino and San Martino, probably done on cotton textile by an anonymous author, was carried out with an unusual technique, i.e., using a monochrome sketch painted with a slight tonal range (Figure 1). The preparation layer, the priming, and the actual painting are in animal glue tempera, and the execution technique is poor and not cohesive, as confirmed by the results of the analysis carried out by Stefano Volpin and discussed subsequently.

Large areas of the painting were water stained, probably because of its original outdoor location. The cleaning intervention served to remove the incoherent dirt from the surface and to resolve the moisture staining problem. Different tests with different materials and methodologies were carried out.

CLEANING PROCEDURE

The first approach to the cleaning was difficult. Every intervention based on aqueous methods resulted in moisture absorption by the surface and the formation of a new water stain where the product was applied. Subsequently, laser cleaning was tested unsuccessfully. Next, different kinds of erasers (kneaded, soft, and stiff erasers) were used, and agar gels were also tested. These were applied with different methodologies, such as (1) pregelatinized agar brushed on small areas (Campani et al., 2007), (2) agar as a stiff gel applied for a few minutes to have the lowest level of water, (3) preliminary saturation of the surface with an alcohol and water mixture airbrushed on the surface prior to the agar application to prevent moisture stains, (4) preliminary saturation of the surface with cyclododecane at different concentrations applied by brush followed with the agar application, and (5) agar reinforced with carboxymethylcellulose to "soften" the material and to adapt it to the painting surface. The most interesting result was obtained using a preliminary application of cyclododecane (60% cyclododecane, 40% petroleum ether [80°–120°C fraction] w/v) to stop water diffusion into the surface, thus preventing moisture stains, followed by a brush application of pregelatinized agar (Hangleiter and Saltzmann, 2008).

***Alberto Finozzi**, **Alessandra Sella**, and **Chiara Stefani**, Restauro Studio, Via Mazzini 43, Schio, Vicenza, Italy. Correspondence: Alberto Finozzi, albertofinozzi@libero.it; Alessandra Sella, alessandra73_4@libero.it; Chiara Stefani, chiara_stefani_4@libero.it.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

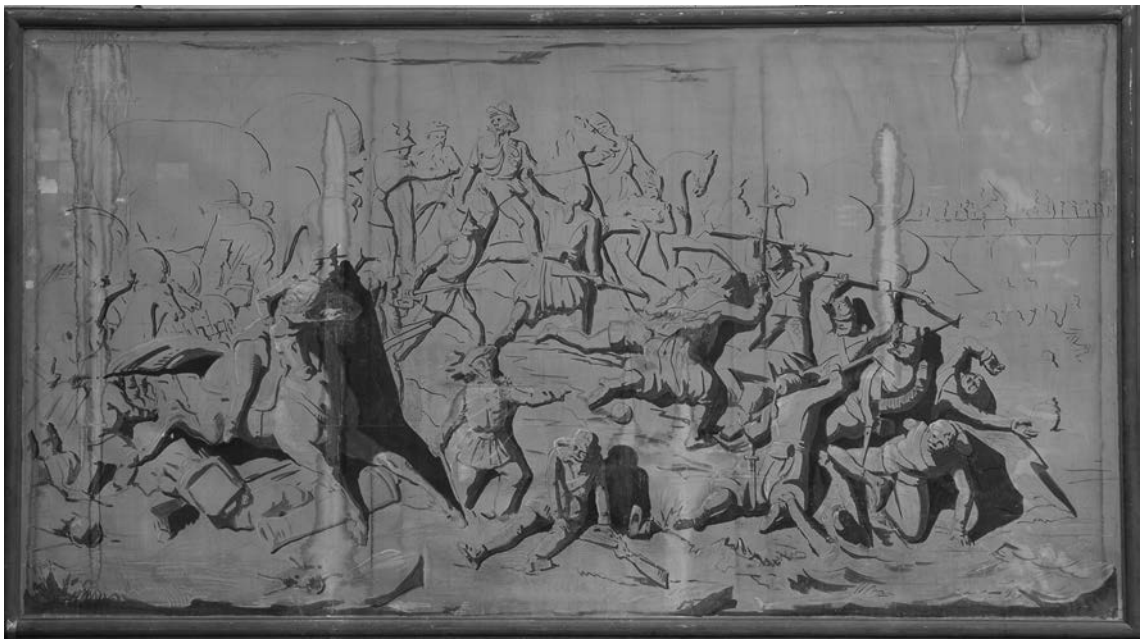


FIGURE 1. Canvas painting of the St. Martin's Battle, showing water staining before cleaning operation.

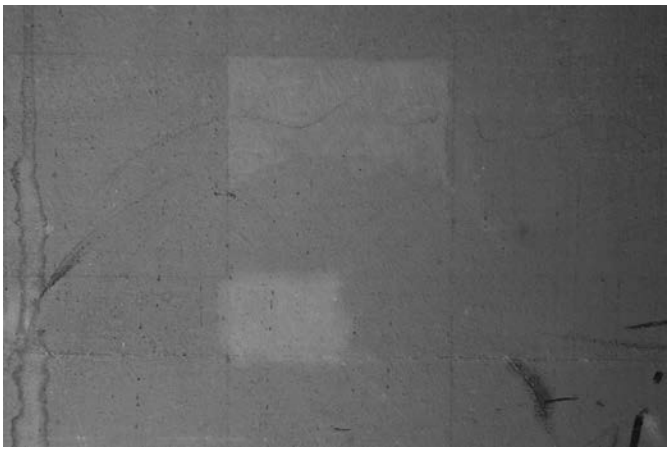


FIGURE 2. Cleaning test examples. On the left. agar gel after the application of cyclododecane proved effective. On the right. the laser proved rather ineffective.

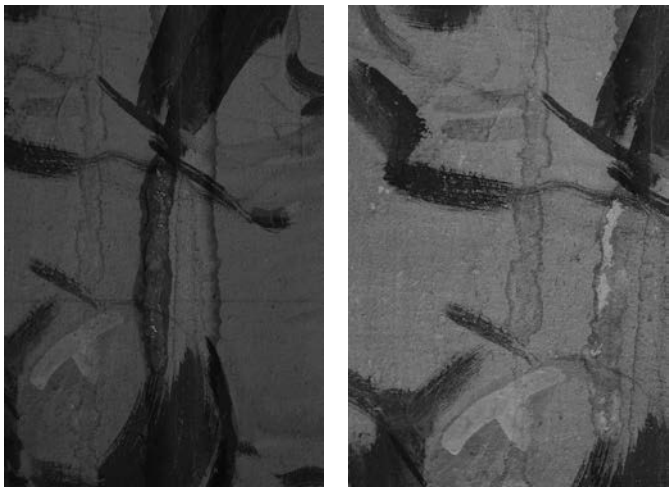


FIGURE 3. (left) Agar gel applied to a water-stained area. (middle) Wet appearance of the surface after the removal of the agar gel. (right) Inhomogeneous appearance of the area after drying.

On areas unstained by water, better results were obtained during the first cleaning tests. The cleaning was more homogenous, the surface dirt removal was effective, and the paint layer was not damaged (Figure 2).

On the other hand, on water-stained areas, different results were obtained. This might have occurred because the surface was weaker, so that even a minimum amount of water was too aggressive to the paint layer. When the agar gel was removed, it ripped off the paint layer in an irregular way, and no uniform results could be obtained (Figure 3).

It is difficult to understand how the contact between two theoretically incompatible materials, i.e., cyclododecane and agar, could result in an effective cleaning operation. As the cyclododecane is a hydrophobic material, it was expected that it would repel the surface water, thus preventing the action of the

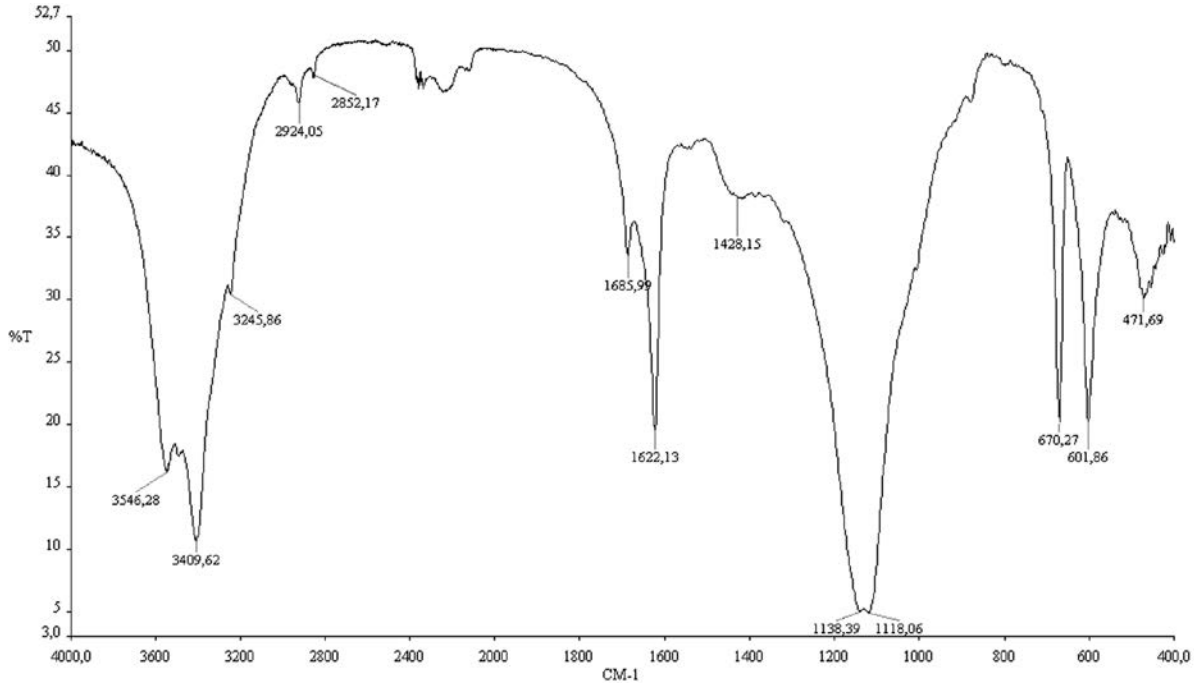


FIGURE 4. The FTIR spectrum showing the presence of gypsum, protenaceous material, and traces of calcium carbonate, identified by the 1400 cm^{-1} peak.

hydrophilic agar (Hiby, 2008; Riggiardi, 2010). It could be hypothesized that the heat produced by the agar gel allowed the interaction of these two materials since it enabled the cyclododecane to reach its melting temperature (58°C–61°C), so that the liquid penetrated into the pictorial layers and enabled the agar to act on the surface.

ANALYSIS OF RESULTS ON THE PREPARATION LAYERS

A small quantity (less than 1 mg) of ground material was scraped from a fringe area of the painting. The aim of the analysis was to identify the composition of the ground material and to observe the morphological structure of the mixture. The sample was analyzed with a micro–Fourier transform infrared spectroscopy (FTIR) and with the aid of some spot tests to identify the type of organic binder.

The ground was made with a mixture of gypsum and a proteinaceous binder, possibly animal glue. The FTIR spectrum shows that apart from gypsum, only traces of calcium carbonate are found but no anhydrite or silica (Figure 4). Spot tests were negative for polysaccharides, i.e., vegetable gums, and for starch, e.g., flour. However, there are some traces of fats. It is evident that the gesso mixture is lacking a binder; the white ground contains mainly gypsum with a very small amount of animal glue. This is probably the real reason for the great fragility shown by the ground.

Acknowledgments

We thank Padua's Culture Councilor for allowing the use of the images in this paper. We also thank Paolo Cremonesi for collaboration during the agar testing, Stefano Volpin for the scientific analysis, and our colleague Daniela Mancin for the translation of the text.

REFERENCES

Campani, E., A. Casoli, P. Cremonesi, I. Saccani, and E. Signorini. 2007. *L'Uso di Agarosio e Agar per la Preparazione di "Gel Rigidi."* [The Use of Agarose and Agar for Preparing "Rigid Gels."] Quaderni Cesmar7, No. 4. Padua: Il prato.

Hangleiter, H. M., and L. F. Saltzmann. 2008. "Volatile Binding Media: Cyclododecane. The Care of Painted Surfaces. Materials and Methods for Consolidation and Scientific Methods to Evaluate Their Effectiveness." In *The Care of Painted Surfaces: Materials and Methods for the Consolidation, and Scientific Methods to Evaluate Their Effectiveness,* ed. Cesmar7, pp. 105–109. Padua: Il prato.

Hiby, G. 2008. *Il ciclododecano nel restauro di dipinti su tela e manufatti policromi.* [Cyclododecane in the Restoration of Canvas Paintings and Polichrome Objects.] Quaderni Cesmar7, No. 5. Padua: Il prato.

Riggiardi, D., ed. 2010. *Il Ciclododecano nel restauro dei manufatti artistici.* [Cyclododecane in the Restoration of Artistic Works.] Quaderni Cesmar7, No. 8. Padua: Il prato.

Dry Cleaning Approaches for Unvarnished Paint Surfaces

Maude Daudin-Schotte, Madeleine Bisschoff, Ineke Joosten, Henk van Keulen, and Klaas Jan van den Berg

ABSTRACT. A range of materials used in conservation practice were selected to perform dry cleaning tests of water- and mechanically sensitive, soiled, and artificially aged paint surfaces. Results were assessed visually, by light and electron microscopy, as well as through gloss measurements based on topography integrity, gloss integrity, clearance of residues, cleaning power, aging stability of residues and paint surfaces after testing, and UV fluorescence changes. Of the tested materials, yellow microfiber cloth, white akapad, and polyurethane-based makeup sponges were shown to be the most efficient and safe materials on different paint surfaces. Groom/stick and Absorene were problematic, especially for underbound, matte paints, leaving resilient hardening residues. Polyvinyl chloride erasers left plasticizer residues, with the potential for softening the paint layer with aging. It was noted that the stability and usefulness of materials such as polyurethane makeup sponges may be compromised if the manufacturer changes their chemical composition.

INTRODUCTION

The removal of dirt from an unvarnished paint surface may be very challenging, especially when the deposit is patchy and resilient or in cases where fragile unvarnished underbound paint surfaces are sensitive to aqueous solvents. In these cases or when the dissolved dirt can impregnate the paint surface irreversibly, alternative nonsolvent cleaning methods are mandatory.

Noncontact methods such as laser cleaning have been proposed but are generally considered both unsafe and too costly for unvarnished paintings. Dry surface cleaning is an alternative that is occasionally practiced by painting conservators, employing a large range of specific materials like sponges, erasers, malleable materials, and microfiber cloths. However, since there is a strong concern about their potential damaging effects on surfaces, these materials have not yet been fully integrated into current practice. Only a few studies have focused on the use of dry cleaning materials in conservation (Wehlte, 1971; Schorbach, 2009), and most of them are related to textile (Estabrook, 1989) and paper conservation (Brokerhof et al., 2002; Noehles, 2002).

A project carried out at the Cultural Heritage Agency of the Netherlands (RCE, formerly known as ICN) in collaboration with painting conservators in the Netherlands and the United Kingdom has aimed at a better understanding of the properties of dry cleaning materials in relation to the physical and optical integrity of the paints (Burnstock et al., 2006; Ormsby et al. 2006; Morrison et al., 2007), the potential for removing any residues off the surface, and the long-term effects of residual materials on the painting. Analytical

Maude Daudin-Schotte *and* ***Madeleine Bisschoff****, Amsterdam, Netherlands.* ***Ineke Joosten****,* ***Henk van Keulen****, and* ***Klaas Jan van den Berg****, Cultural Heritage Agency of the Netherlands, P.O. Box 76709, 1070 KA Amsterdam, Netherlands. Correspondence: Maude Daudin-Schotte, dsconservation@free.fr; Madeleine Bisschoff, madeleinebisschoff@gmail.com; Klaas Jan van den Berg, k.van.den.berg@cultureelerfgoed.nl.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

and practical investigations of the dry cleaning materials have shed light on the nature and potentially detrimental effects of the materials (van Keulen et al., 2010).

This paper presents the testing methodology and results of dry cleaning materials on underbound and solvent-sensitive surfaces (E. Froment, University of Amsterdam, unpublished internal report, "Cleaning Workshop: A Collaboration between Amsterdam University and the Cultural Agency of the Netherlands," 2009 and M. Daudin-Schotte, Cultural Heritage Agency of the Netherlands, unpublished internal report from the 2006–2009 Research Project "Application of Dry Cleaning Methods on Unvarnished Modern Paintings," 2010). The results are discussed in the light of cleaning effectiveness related to topography changes and potentially harmful residues.

EXPERIMENTAL METHODS AND MATERIALS

Cleaning Materials

After preliminary cleaning tests on soiled and artificially aged oil paint surfaces with more 20 cleaning materials used in conservation (Daudin-Schotte, 2010; Van Keulen et al., 2010), a selection of the best performing and most commonly used materials was chosen for further research (see Table 1). The materials' composition was obtained through chemical analysis (H. van Keulen, M. Groot Wassink, S. de Groot, I. Joosten, M. Daudin-Schotte, M. van Bommel, and K. J. van den Berg, Cultural Heritage Agency of the Netherlands, unpublished data) and from manufacturers' data sheets.

Aging procedures were performed for 4–6 weeks at temperatures of 50°C–60°C and relative humidity (RH) variations from 27% to 70%–80% every six hours. Light aging was carried out with fluorescent tubes (10,000 lux) for approximately 600 hours at a temperature of 23°C and RH of 44%, equivalent to 11.5 years of aging under museum conditions, assuming reciprocity. The aim was to assess each cleaning material's stability as well as potential changes to paint surfaces from residues after each cleaning test.

Paint Surfaces

Test samples were organized in three series, using canvas prepared on cardboard.

I. The first series of tests were performed on a naturally aged 30-year-old monochrome oil painting on canvas (van den Berg et al., 2008). The top paint layer consisted of a monochrome light green oil painting containing zinc, lead, and titanium white with a barium sulfate filler in addition to two as yet unidentified organic yellow pigments. A very thin strongly fluorescent surface layer is visible under UV light, possibly a skin of the medium.

II. Water-sensitive cadmium red, cadmium yellow, and ultramarine blue tube oil paints from Talens Rembrandt Artists' Quality (Mills et al., 2008) were painted out on artists' boards, cured in ambient conditions for four months, and artificially aged for 2,700 hours at 10,000 lux at room temperature. After aging, the samples were stored at ambient conditions for 4 months, soiled with dust collected from the cellar of the ICN building, and stored in a greasy environment (the kitchen of the ICN Ateliergebouw) for 4 months.

III. Gouache samples were painted out on artists' boards, mixing one measure of tube paint of Talens ECOLA Plakkaatverf with the same measure of pure pigment from Verfmolen "De Kat" (Zaandam, Netherlands) to produce slightly underbound matte surfaces (cadmium red, cadmium yellow, and ultramarine

TABLE 1. Dry cleaning materials tested in this study. Each test was followed by brushing and vacuuming of the surface.

Type	Product Name	Picture	Composition[a]	Application	Manufacturer/ Suppliers	Description (observed when tested)
Malleable materials	Absorene		Filler: starch; solvent: white spirit	Rolled with hand over the surface, in tube shape	Absorene Company Inc (England)	Quite sticky, malleable
	Groom/stick		Isoprene rubber, chalk	Applied rolled around a wooden stick like a cotton swab	Picreator Enterprises Ltd. (England)	Very sticky, malleable.
Erasers	Edding R10		Polyvinyl chloride (PVC), di-isooctyl phthalate (DIOP)	Applied with a minimum pressure, in circle movements	Local stationers (international)	Relatively hard material; harder than Pentel ZF11 and Bic Galet

(*continued*)

TABLE 1. (*Continued*)

Type	Product Name	Picture	Composition[a]	Application	Manufacturer/ Suppliers	Description (observed when tested)
Erasers	Pentel ZF 11		Polyvinyl chloride PVC), phthalates (DIOP, DMP, MEHP); butoxytriglycol, dioctylazelate; chalk	Applied with a minimum pressure, in circle movements	Stouls (France)	Relatively hard material; harder than Bic Galet
	Bic Galet		Factis (vulcanized vegetable oil) chalk	Applied with a minimum pressure, in circle movements	Local stationers (international)	Softest eraser with highest amount of crumbs
Cloths	Yellow micro-fiber cloth		Polyethylene terephthalate (PET); polyester: Nylon 6 (polyamide)	Folded and applied in figure eight shape movements	Blokker, local drugstore (Netherlands)	Nonwoven cloth.
Sponges	Smoke sponge		Isoprene rubber, sulfur chalk, not completely vulcanized natural rubber	Applied with a minimum pressure, in circular movements	Conservation by design Ltd. (England)	Rubbery texture, flexible material.
	Akapad White		Styrene butadiene rubber (SBR), vulcanized castor oil, antioxidant NG-2246	Applied with a minimum pressure, in circular movements	Akachemie, Deffner & Johann (Germany)	Self-consuming material, more compact than Akapad yellow
Makeup sponges	Etos (white, triangle shape)		Isoprene rubber, butylated hydroxytoluene (BHT)	Piece of sponge applied in figure eight shape movements and slight pressure; used as obtained and rinsed in demineralized water prior to use	Etos stores (Netherlands)	Very soft and flexible texture
	Hema (white, triangle shape)		Styrene butadiene rubber (SBR), butylated hydroxytoluene (BHT), diethyldithiocarbamate mercaptobenzothiazole	Piece of sponge applied in figure eight shape movements and slight pressure; used as obtained and rinsed in demineralized water prior to use	HEMA stores (Netherlands)	Very soft, flexible texture, comparable to isoprene rubber make-up sponges
	QVS (white, triangle shape)		Polyurethane ether (TDI)	Piece of sponge applied in figure eight shape movements and slight pressure; used as obtained and rinsed in demineralized water prior to use	Probably discontinued product, QVS, drugstores (England)	Very soft and flexible
Gum powder	Draft clean powder		Yellow particulates: styrene butadiene rubber (SBR); brown particulates: factis	Sprinkled over the surface; cotton pad was used with even and soft application	Conservation by Design Ltd. Archival aids (England)	Differences in particulate sizes depending on the brand

[a]Composition information is from ICN Web site table; see text.

blue were used to allow optical comparisons with series II). Samples were soiled as in series II.

Dry Cleaning Tests

Cleaning tests were performed under ambient temperature and humidity (±22°C at 50% RH) at the ICN laboratories. After each test the paint samples were brushed and vacuumed. Test results were first observed visually (normal light, UV fluorescence, raking light) and then with light microscopy (polarized light, UV fluorescence, raking light), followed by electron microscopy (low vacuum, acceleration voltage from 1.7 to 20 kV, backscattered electron and low-vacuum secondary electron at magnifications of 100× to 2500×). Gloss measurements were performed to complete microscopic visual assessment. The following pieces of equipment were used: a ZEISS Axioplan 2 light microscope with ZEISS neofluar lenses and Axiovision 4.4 software, a Jeol JSM 5900 lV scanning electron microscope (SEM), a Tri-glossmaster 20-60-85 glossmeter from SHEEN, and a Sony Cybershot DSC-F505V digital camera.

Observations were recorded in evaluation tables (Table 2) with attention to six criteria: topography integrity, gloss integrity, removal of residues, cleaning power, stability of the paint surface after testing and after artificial aging, and (if applicable) UV fluorescence changes. The syntheses of the results were then represented in star diagrams (Figure 1).

RESULTS

The results of the experiments on the water-sensitive oil and gouache paints are presented in Table 3.

TABLE 2. Example of the evaluation table used in this study: Results of the Absorene tested on the cadmium red gouache. Grades are from 0/10 (null) to 10/10 (excellent). — = no data

Tested materials	Topography integrity	Gloss integrity	Change under UV light	Clearance of residues (per cm^2)	Cleaning power	Stability with aging
Number 3: Absorene[b]	Abrasion (10/10)	5/10 (significant decrease in gloss)	None	Quantity on the picture spot (film deposit)	Evenness (5/10)	Change in color: more cloudy and gray
	Polishing (9/10)	5/10 (significant decrease in gloss)	None	Color (—)	Paint layer (6/10)	Change in color: more cloudy and gray
	Flattening (8/10)	5/10 (significant decrease in gloss)	None	Size (—)	Crumbs (—)	Change in gloss: more matte
	Cracks and holes (10/10)	5/10 (significant decrease in gloss)	None	Tenacity (—)	Material (3/10)	Other: thin, hard skin impregnated into the paint layer
	Global evaluation: 9.4/10	Global evaluation: 5/10	Global evaluation: None	Global evaluation: 1/10	Global evaluation: 5/10	Global evaluation: 1/10

[a] Increase or decrease, observed with the naked eye.
[b] Cleaning achieved for a 2 minute application and 5 s vacuuming and brushing (if no dust remains, it becomes stickier).

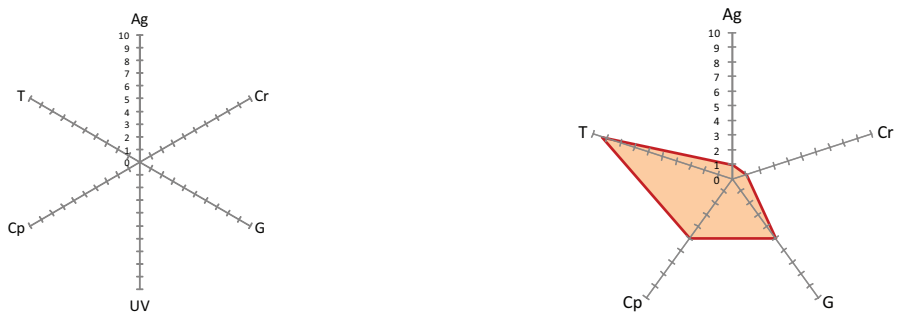
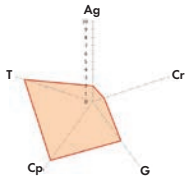
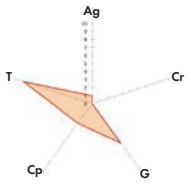
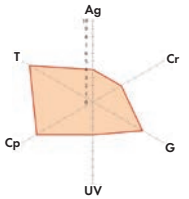
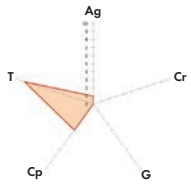
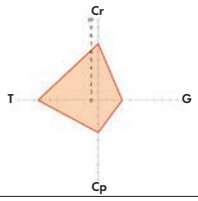
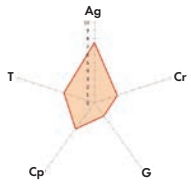
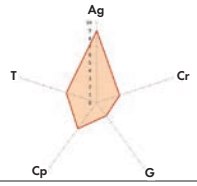
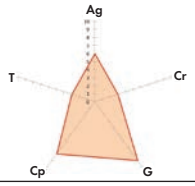
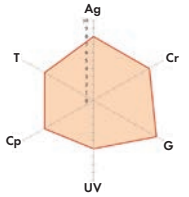
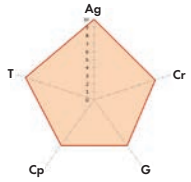
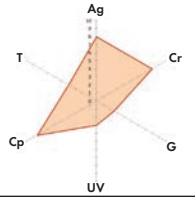
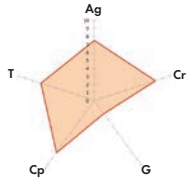


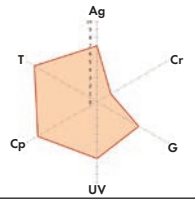
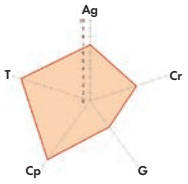
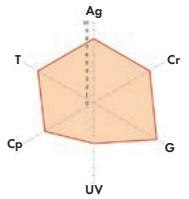
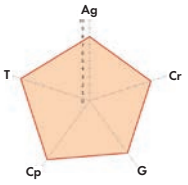
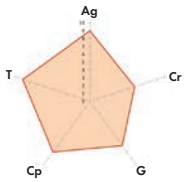
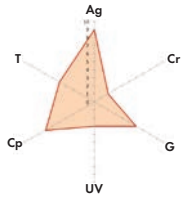
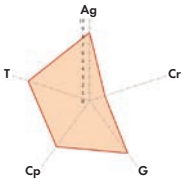
FIGURE 1. Star diagram examples. (left) Not filled in. Note that 0/10 corresponds to an extremely poor result, and 10/10 corresponds to an excellent test result. T = topography integrity; Ag = stability of paint surface after testing and artificial aging; Cp = cleaning power; Cr = clearance of residues; G = gloss integrity. (right) Example of a star diagram with Absorene scores from tests on gouache (see Table 2).

TABLE 3. Average dry cleaning test results on oil paint (sample II) and gouache (sample III). T = topography integrity; Ag = stability of paint surface after test and after artificial aging; Cr = clearance of residues; G = gloss preservation; UV = preservation of the paint layer aspect under UV fluorescence; Cp = cleaning power. See Table 1 for materials images.

Material class	Material name	Average result on series II (oil paint layer sensitive to water)[a]	Average result on series III (underbound gouache paint layer)[a]	Handling remarks	Observations after aging (indication of aging tendencies of residues)
Malleable	Absorene				The "pink plasticine" became rock hard; an oily substance was leached out during the aging process, mixed with a very hard translucent substance (gray crystals)
	Groom/stick			Rolled around wooden stick for ease of use	Much stickier after aging and still glossy; it has softened into a liquid shape; on very thin areas, it became translucent and matte, like a little gray skin (this corroborates its aging on paint surfaces)
Erasers	Edding R10				A little bit yellower and less flexible
	Pentel ZF11	Not tested			It generated a little bit of oily substance during aging; the eraser is also slightly less flexible
	Bic Galet		Not tested		No change
Cloths	Yellow microfiber cloth			Cloth with velvety characteristics, quite thick; produces threads when cut off	No change
Sponges	Smoke sponge			Greasy surface becomes harder and unusable within months; store protected from air	More compact, less flexible, harder, and yellower than before aging.

(*continued*)

TABLE 3. (*Continued*)

Material class	Material name	Average result on series II (oil paint layer sensitive to water)[a]	Average result on series III (underbound gouache paint layer)[a]	Handling remarks	Observations after aging (indication of aging tendencies of residues)
Sponges	White Akapad			Soft contact with paint layer	Slightly more compact, yellower on one side; otherwise, it remains comparable with brand new Akapad
Make-up sponges	Etos rinsed (isoprene rubber)			Strong yellowing when rinsed with demineralized water	Much more yellow and harder
	QVS rinsed (polyurethane ether)	Not tested		Swells in water during rinsing; becomes less compact and even more flexible after rinsing and drying	Overall comparable with a nonaged rinsed QVS, although it has become slightly less flexible than before aging
Gum powder	Draft clean powder DCP3			Sprinkled over the surface; cotton pad was used to evenly and softly scrub	The smallest particulates became slightly stickier; the other particulates remain comparable to the brand new gum powder

[a] Number of axes depends on the relevance of each criterion during tests.

Abrasion and Polishing versus Cleaning Efficacy

For all materials, except the malleable class, the mechanical action is the basic cleaning principle, which implies close contact between the cleaning material and paint surface. As a result, potential damage, such as abrasion, flattening, and polishing of the surface topography, is particularly pertinent.

The test results show that the Akapad white and makeup sponges were the least abrasive polishing materials. Both materials were very efficient as well, especially Akapad for the removal of embedded and resilient dirt. Figures 2 and 3 show light microscopy and SEM results for the polyurethane QVS sponge tested on a cadmium yellow gouache paint sample.

In contrast, and as perhaps suspected, the erasers (PVC or factis based) proved to be the most harmful materials (Figure 4). Tests on paint sample I, oil paint, resulted in a strong loss of UV fluorescence because of abrasion of the skin of medium (Figure 5) as well as rubbing on the topography (clearly visible in SEM images; Figure 6). Furthermore, after testing on series II and III, surface scratches were observed with light microscopy (see Figure 4).

Residual Materials from the Cleaning Agents: Crumbs and Stability with Aging

In addition to issues of mechanical abrasion, what is of great concern, even if less visible, is the potential long-term detrimental action of the residue from the cleaning materials left as a sticky particulate residue or as a film of material. Assessments were made on the basis of the chemical analysis of tested paint surfaces as well as visual observations, taking into account the

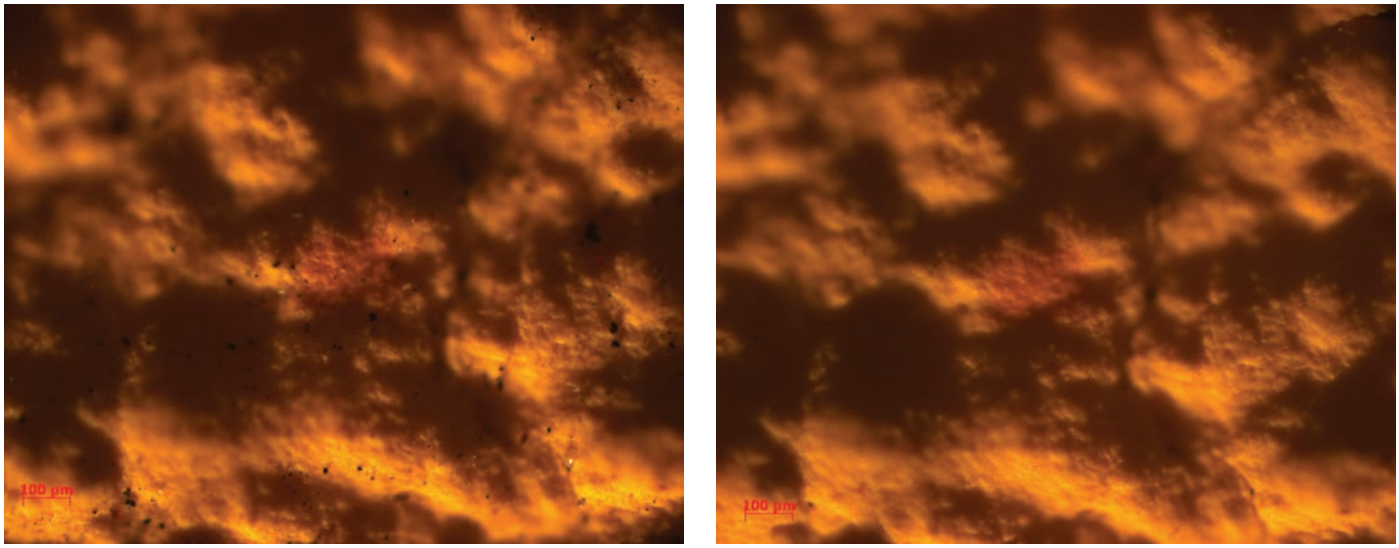


FIGURE 2. Cadmium yellow gouache sample, (raking) light microscopy at 100× magnification, (left) before and (right) after testing with rinsed polyurethane ether makeup sponge (QVS). The topography is preserved, which is confirmed with SEM observations (Figure 3) .

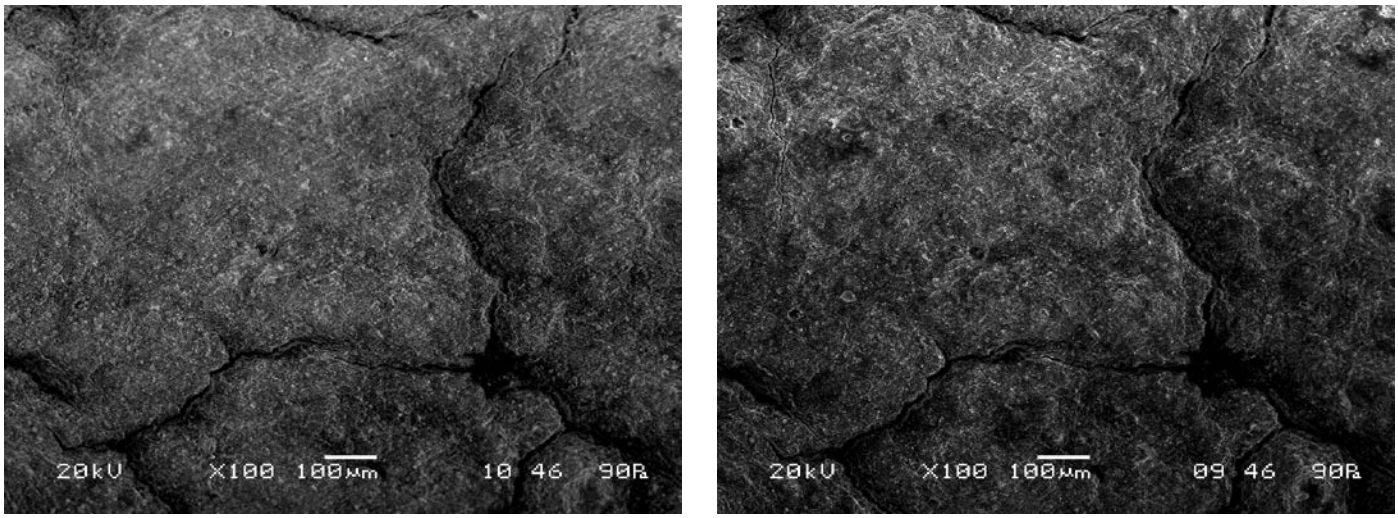


FIGURE 3. Cadmium yellow gouache sample, (left) before and (right) after testing with rinsed polyurethane ether makeup sponge (QVS); SEM images (LSEI mode) at 100× magnification.

extractable components that are potentially harmful to the paint surface.

Chemical residues were only detected in test samples treated with PVC erasers, for which plasticizers were detected (van Keulen et al., in preparation). This is of concern since plasticizers can soften the paint surface, leaving it more sensitive to dust and vulnerable to abrasion or polishing.

Groom/stick and Absorene were found to leave a film deposit or particulate residue on both well-bound and porous paint layers (see Figures 7, 8, and 9), which proved to harden and embed into the paint layer with aging. This was also observed with kneaded gums and gum powders, albeit to lesser degrees.

With an average maximum of 2 particles/cm^2, makeup sponges, smoke sponges, and cloths left the least particulate residue while achieving a generally good cleaning level. These materials also age relatively benignly. No chemical residues are expected to be left by cloths, and none were detected analytically on the paint samples treated with smoke sponges.

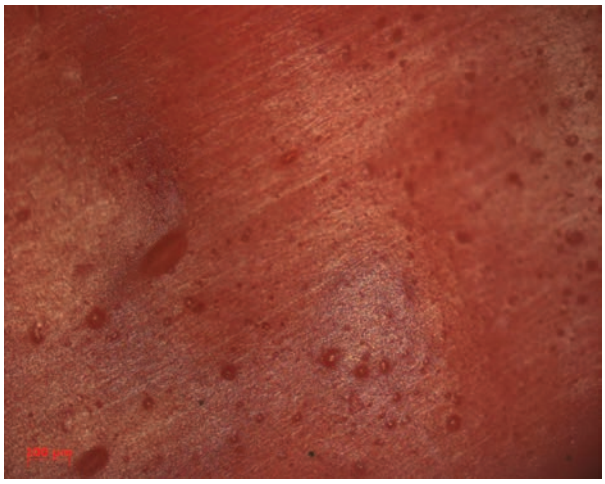


FIGURE 4. Local abrasion with scratches observed on red cadmium oil paint surface tested with a Bic Galet (series II) eraser.

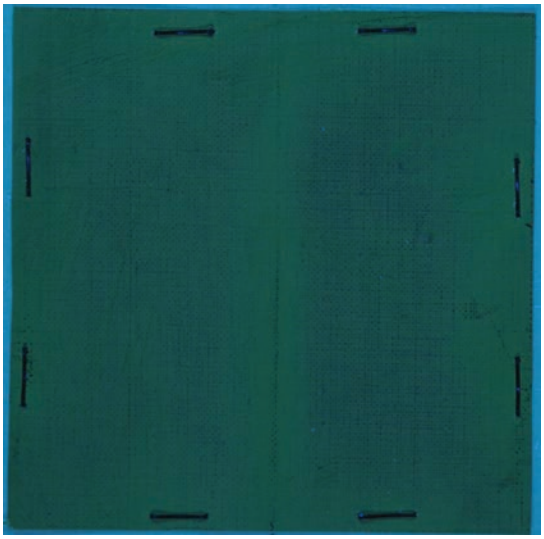


FIGURE 5. Oil paint sample after (left) one- and (right) three-minute tests with a Magic Rub PVC eraser, showing a strong decrease in UV fluorescence in treated areas (series I).

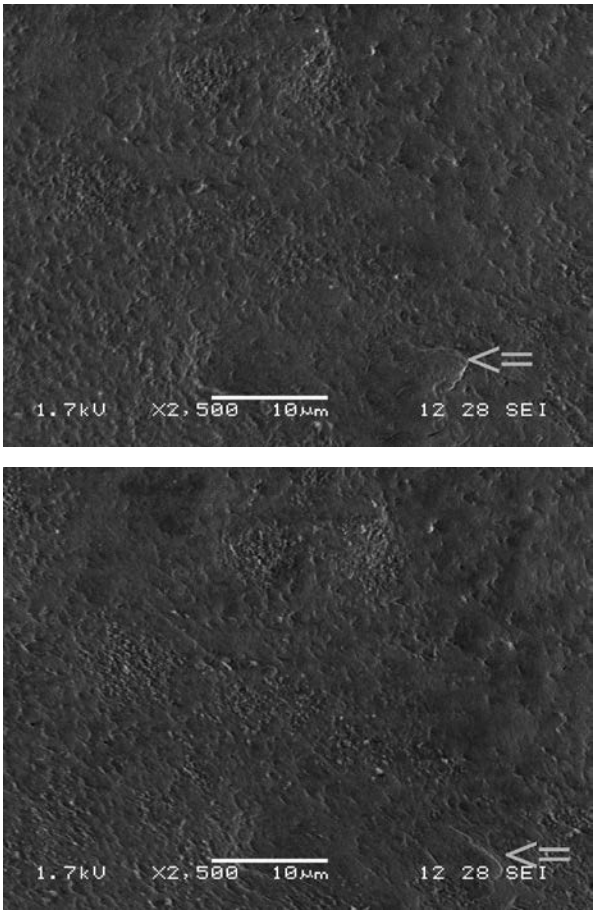


FIGURE 6. Series I Magic Rub eraser test performed on an oil paint sample, SEM SE 2500× magnification. (top) One-minute test and (bottom) three-minute test. The polishing of the surface has clearly increased with increased rubbing time; note the change in the micro-relief (bottom right corner).

DISCUSSION AND CONCLUSIONS

Treatment Purpose versus Optimum Preservation of Surfaces Characteristics

Dry cleaning by rubbing the surface will cause friction and may cause abrasion, flattening, or polishing of the surface depending on the specific mechanical properties of the material. This is avoided by malleable materials, which exhibit a different mechanical behavior but carry the risk of leaving relatively resilient material residue on the surface.

Of all the cleaning materials tested, makeup sponges proved to be efficient and among the safest materials to use. The fine structure and softness of these sponges, primarily produced for skin cosmetic application, enhance their use for gentle dirt removal from delicate surfaces. Most makeup sponges are produced from isoprene, styrene butadiene rubber (SBR), and mixtures of both on an industrial scale. The analyzed SBR-isoprene sponges all contain antioxidants and accelerators used in the rubber-making process. A minor part of the sponges consists of polyurethane, which contains hardly any additives.

A disadvantage is that the availability and/or composition of makeup sponges cannot be guaranteed because of potential changes in composition during manufacturing. For example, the additive-free QVS sponge successfully tested in this study

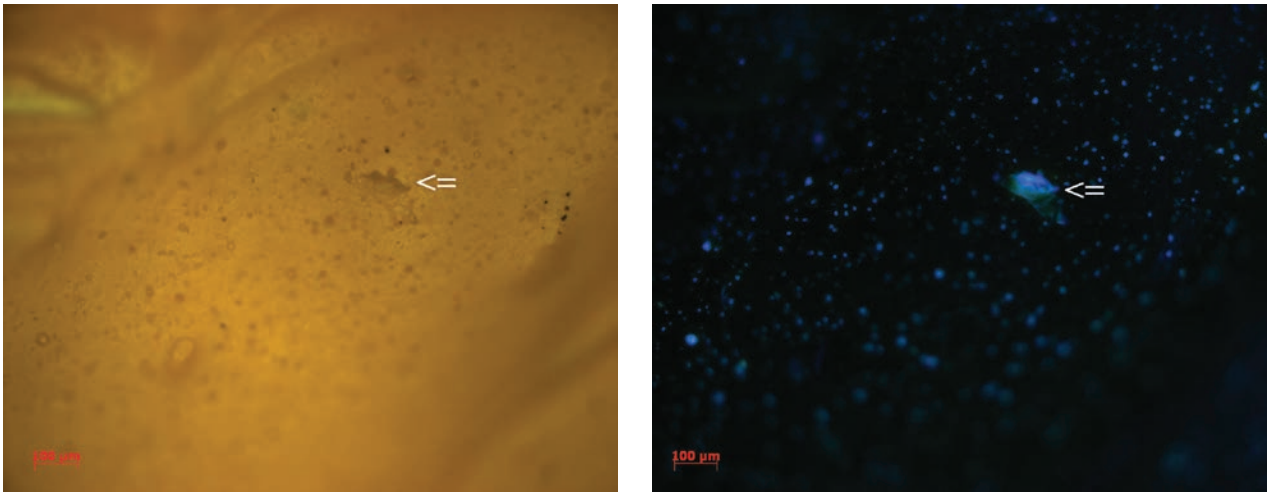


FIGURE 7. Test performed on a cadmium yellow oil paint sample with Groom/stick, with residual material observed with light microscopy: (left) polarized light and (right) UV fluorescence.

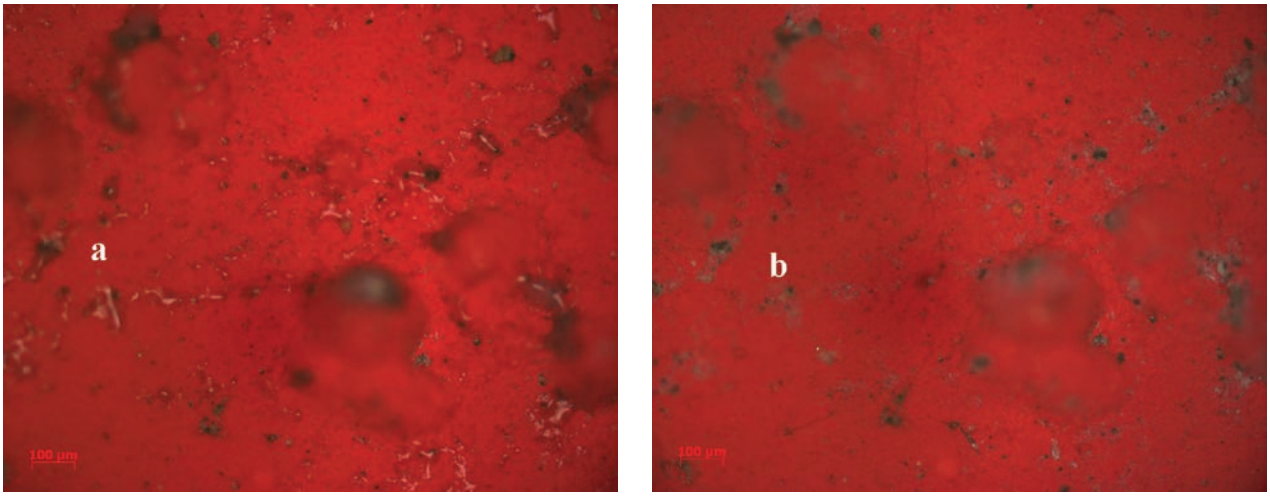


FIGURE 8. Test performed on a cadmium red gouache sample with Groom/stick, light microscopy with polarized light. (a) Appearance before aging, with blackish particulate residues left after testing, and (b) appearance after dark aging, with particulate residues dried and partly embedded in the superficial layer, combined with dirt.

appears to be no longer available on the market. Instead, the polyurethane ether-based HD sponge from Make-up For Ever (composition: polyurethane ether, Tinuvin; see http://www.makeupforever.com/#/int/en/products/tools/sponge-puff/hd-sponge/) has replaced it (this was not tested on all sample sets, but when tested, it showed comparable or even better performance than QVS and HEMA). The HD sponge only contains Tinuvin, a UV light stabilizer, as an additive. As a precaution for removal of possible additives, all makeup sponges were rinsed for 15 minutes in demineralized water and dried well before use (e.g., by pressing them between tissue paper sheets). Although the main part of their organic additives will not dissolve in water, any soluble ones could possibly be transported to the surface of the sponge and be absorbed by the tissue paper.

Of course, in reality dirt and paint surfaces may vary considerably from any test surfaces, and the combinations used in this study may represent only a small portion of those possible. The choice of dry cleaning material depends on the paint layers' characteristics, whether physical (porous, flaking paint, well bound, underbound) or aesthetical (monochrome, colored zones,

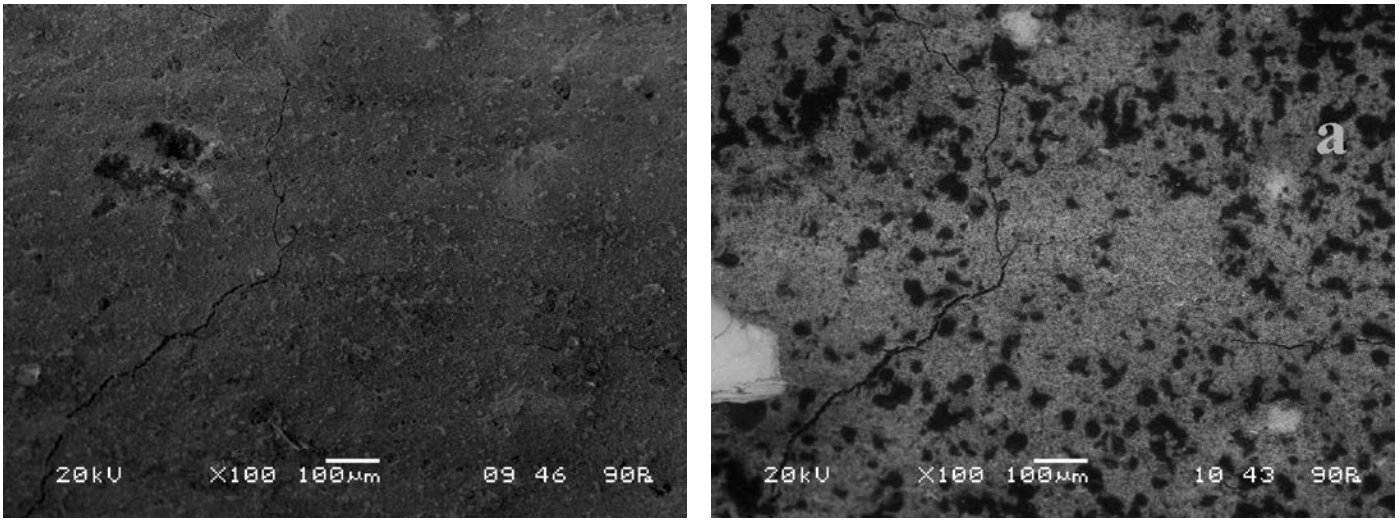


FIGURE 9. Test performed on a cadmium red gouache sample with Absorene; SEM images (low-vacuum secondary electron mode). (left) Before testing and (right) after testing. Numerous Absorene particulate residues are present as dark (organic material) stains (a).

flat, impasted, matte, glossy), and the type of dirt (impregnated, dry, fat, smooth, or grainy).

In addition, different parameters, such as handling and structure, of the dry cleaning material, e.g., even or uneven, absorbent, or malleable, interfere with the cleaning process and influence the results. Considering this, the cleaning tests gave good insight into the working properties and potentially harmful side effects of cleaning materials, with some proving applicable in conservation. On the basis of these observations and considerations, every conservator has to achieve an optimal balance of acceptable results for each specific treatment, as there is no general, straightforward approach for cleaning surfaces with dry materials. To assist in this process, a gradual test approach is presented in the Practical Guidelines section.

Practical Guidelines

For all kinds of paint layers the following materials can be used: (1) polyurethane ether-based makeup sponges (rinsed with demineralized water), (2) yellow microfiber cloths, (3) Akapad white, and (4) smoke sponges (for semiglossy to glossy paint layers only). Additional precautions are as follows:

- In case of granular dust, brush and vacuum clean before dry cleaning.
- Use brand-new materials only to avoid abrasions caused by a degraded surface and unstable residues from old materials.
- Brush surface thoroughly after using Akapad white (at least three times) to remove particulate residues.
- For all sponges, use them only in precut small piece to reduce the amount of residue.
- Rinse these small pieces of makeup sponges for 15 minutes in demineralized water and dry well before use (e.g., by pressing them between sheets of tissue paper).

Acknowledgments

The authors thank the following colleagues for their help: Marjolein Groot Wassink, Suzan de Groot, Luc Megens, Polly Saltmarsh, Maarten van Bommel, Beatriz Veríssimo Mendes, Bill Wei (RCE); Liesbeth Abraham (Frans Hals Museum); Lydia Beerkens (freelance conservator); Zeph Benders (RCE); Aviva Burnstock (Courtauld Institute of Art); Elisabeth Bracht, Rebecca Timmermans, and Louise Wijnberg (Stedelijk Museum Amsterdam); Emilie Froment (Universiteit van Amsterdam); and Kathrin Kirsch (Restauratie Atelier Amsterdam).

REFERENCES

Brokerhof, A. W., S. de Groot, J. L. Pedersoli, H. van Keulen, B. Reissland, and F. Ligterink. 2002. Dry Cleaning: The Effects of New Wishab Spezialschwamm and Spezialpulver on Paper. *Papierrestaurierung,* 3(2):13–19.

Burnstock, A., K. J. van den Berg, S. de Groot, and L. Wijnberg. 2006, "An Investigation of Water-Sensitive Oil Paints in 20th Century Paintings." In *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*, ed. T. Learner, P. Smithen, J. W. Krueger, and M. R. Schilling, pp. 177–188. Los Angeles: The Getty Conservation Institute.

Estabrook, E. 1989. Consideration of the Effect of Erasers on Cotton Fabric. *Journal of the American Institute for Conservation,* 28(2):79–96. http://dx.doi.org/10.2307/3179482.

Mills, L., A. Burnstock, S. de Groot, L. Megens, M. Bisschoff, H. van Keulen, F. Duarte, and K. J. van den Berg. 2008. "Water Sensitivity of Modern Artists' Oil Paints." In *Preprints ICOM-CC 15th Triennial Conference, New Delhi,* Volume 2, ed. J. Bridgland, pp. 651–659. New Delhi: Allied Publishers.

Morrison, R., A. Bagley-Young, A. Burnstock, K. J. van den Berg, and H. van Keulen. 2007. An Investigation of Parameters for the Use of Citrate Solutions for Surface Cleaning Unvarnished Paintings. *Studies in Conservation,* 52: 255–270.

Noehles, M. 2002. Die Kunst des Radierens. Radiermittel im Überblick. [The Art of Erasing. An Overview of Erasers.] *Papier Restaurierung,* 3(1):22–28.

Ormsby, B., T. Learner, M. Schilling, J. Druzik, H. Khanjian, D. Carson, G. Foster, and M. Sloan. 2006. The Effects of Surface Cleaning on Acrylic Emulsion Paintings—A Preliminary Investigation. In *Oberflächenreinigung: Materialien und Methoden,* ed. Cornelia Weyer, pp. 135–149. VDR Schriftenreihe 2. Stuttgart, Germany: Theiss Verlag.

Schorbach, S. 2009. Reinigungsschwämme in der Restaurierung—Vergleichende Untersuchung zu Material, Wirkung und Rückständen. [Cleaning Sponges in Restoration—A Comparative Study with Regards to Material, Effectiveness and Conditions.] *Zeitschrift für Kunsttechnologie und Konservierung,* 23(1): 41–54.

van den Berg, K. J., M. Daudin, I. Joosten, W. Wei, R. Morrison, and A. Burnstock. 2008. "A Comparison of Light Microscopy Techniques with Scanning Electron Microscopy for Imaging the Surface Cleaning of Paintings." Paper presented at the 9th International Conference on NDT of Art, Jerusalem, 25–30 May. http://www.ndt.net/article/art2008/papers/033VandenBerg.pdf (accessed 16 November 2012).

van Keulen, H., S. de Groot, M. Groot Wassink, I. Joosten, K. J. Van den Berg, and M. Daudin. 2010. Dry Cleaning Products Analysed and Tested at the Netherlands Institute of Cultural Heritage. http://www.cultureelerfgoed.nl/sites/default/files/documenten/drycleaning%20table-26-jan-2011.pdf (accessed 19 November 2012).

Wehlte, K. 1971. Trockenreiniger für Tafelgemälde und Wandmalerein. [A Dry Cleaning Material for Panel and Wall Paintings.] *Maltechnik,* 77:10–13.

Extended Abstract—The Schlürfer: A Vacuum Technique for the Cleaning of Paintings

Ina Hausmann and Petra Demuth

INTRODUCTION

In the early 1990s, the Schlürfer (from the German *schlürfen*, to slurp) was developed for dirt removal from sensitive modern art paintings by the German conservator Winfried Heiber (Nicolaus, 1998), later professor at the Academy of Fine Arts in Dresden. It was initially used for unvarnished paintings, where the traditional mechanical methods of water-based cleaning (such as rolling, wiping, and swabbing with wet soft sponges, tissues, or cotton swabs) led to pigment loss, color changes, and microdeformations. In contrast, a water treatment with the Schlürfer was able to reduce the mechanical impact to the extent that no paint damage or negative effects could be observed.

EQUIPMENT DESCRIPTION

The Schlürfer equipment (see Figure 1) can be described as follows: a vacuum pump equipped with a regulator and gauge is connected to a gas-washing bottle (optionally fitted with a filter disc to reduce the size of air bubbles) via a flexible hose. Another flexible hose, the "working" one, is connected to the other side of the gas-washing bottle and has a soft moistened suction PVA sponge (a highly absorptive, microporous sponge essentially composed of polyvinyl alcohol) at its end. Because of the suction of the vacuum pump, the solubilized dirt is vacuumed through the soft wet sponge during the cleaning process. Dirt and solvent are collected in the water-filled gas-washing bottle. A cotton filter pad (optionally containing sodium chloride) in front of the outlet is generally recommended to protect the pump. The elements of the Schlürfer, e.g., gas-washing bottle volume, sponge size, hose diameter, and length, etc., have to be modified according to specific characteristics of the painting and the substances to be removed. Standard sizes are around 3 cm diameter sponge (4 cm in height), a 0.5 cm diameter hose, and a 500 mL gas-washing bottle.

Instead of a mechanical interaction with cotton swabs, tissues, etc., water is applied to the paint surface with a fine soft flat brush. Immediately after water contact, the solubilized dirt is vacuumed, keeping friction and abrasion to a minimum. The technique offers the option of a short intensive water application. Because the suction power of the Schlürfer is much higher than that of sponges, cotton fibers, microfiber tissues, etc., the water can be removed rapidly from the surface.

***Ina Hausmann**, Prinzessinnenstrasse 16, 10969 Berlin, Germany. **Petra Demuth**, Cologne Institute of Conservation Sciences, Cologne University of Applied Sciences, Ubierring 40, 50678 Cologne, Germany. Correspondence: Ina Hausmann, ina.hausmann@yahoo.de; Petra Demuth, petra.demuth@fh-koeln.de.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

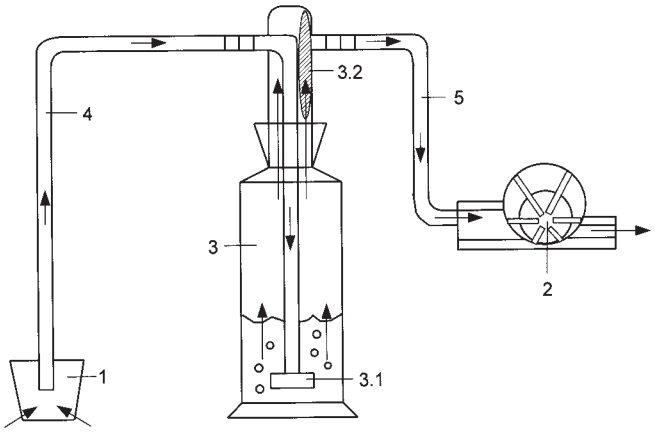


FIGURE 1. The Schlürfer apparatus: (1) soft wet sponge, (2) vacuum pump with a controller and gauge, (3) water-filled gas washing bottle, with a filter disc (3.1) and cotton filter pad (3.2), and (4 and 5) two flexible hoses.

PRACTICAL APPLICATION

Apart from its original use for dirt removal, the Schlürfer also can be used for varnish removal. In the following case study, an aged polyvinyl acetate (PVAc) coating on a matte porous glue-based frail paint layer was removed with the help of this apparatus. In 1914, Ernst Pasqual Jordan and Richard Schlösser painted an ensemble of 12 landscapes and town views for the town hall in Buxtehude, Germany. These naïve romantic paintings, typical for the time, are picturesque decorations of an ideal world in bright colors (Figure 2). Possibly during the 1930s, a glossy, thick layer of an aqueous polyvinyl acetate emulsion was brushed on. This turned yellow and gray with time. As a result, the typical visual impression of light, pastel-like paintings on fibrous tightly woven canvases was completely lost.

The aim of the treatment was to regain the original color intensity and matte appearance without endangering the thin and fissured paint layer. For the removal of the aged PVAc varnish, acetone was the strongest and most effective solvent among the various organic solvents tested. However, neither a cotton swab nor solvent gel nor solid poultices led to satisfactory results in comparison with this solvent. The removal of the soluble and/or swollen synthetic resin out of the porous paint layers from the highly absorbent canvas was successfully achieved with the Schlürfer and acetone, but with following modifications (Figure 3).

An intermediate layer of fine Japanese paper (Manila 10 g/m²) was used. After the application of the acetone with a brush on the paper, the wet Schlürfer sponge was pressed onto the surface, and the solubilized polymer was vacuumed through the paper. The removal effect was improved because the PVAc varnish material adhered to the paper. An advantage of using the Schlürfer was that the penetration of the highly viscous solution deeper into the cracks and pores of the paint layers and the textile support could be prevented. Important in this procedure was the close contact of the paper to the paint surface by using a special comb for pressing down the paper. Immediately after the swelling and suction procedure, a transparent plastic film (cling wrap) was applied on to the paper surface with light brush strokes. In this way the tacky PVAc material adhered to the film and could be peeled off as in the strappo technique, resulting in an increased amount of PVAc material removed. Finally, the Japanese paper was removed with acetone.

FIGURE 2. One of the twelve paintings by Jordan and Schlösser in the town hall in Buxtehude, Germany. Photo shows condition before treatment.

The complete treatment had to be repeated three times. The result was an even, homogenous, and extensive reduction of the PVAc varnish (Figure 4). No disturbing white blanching effects

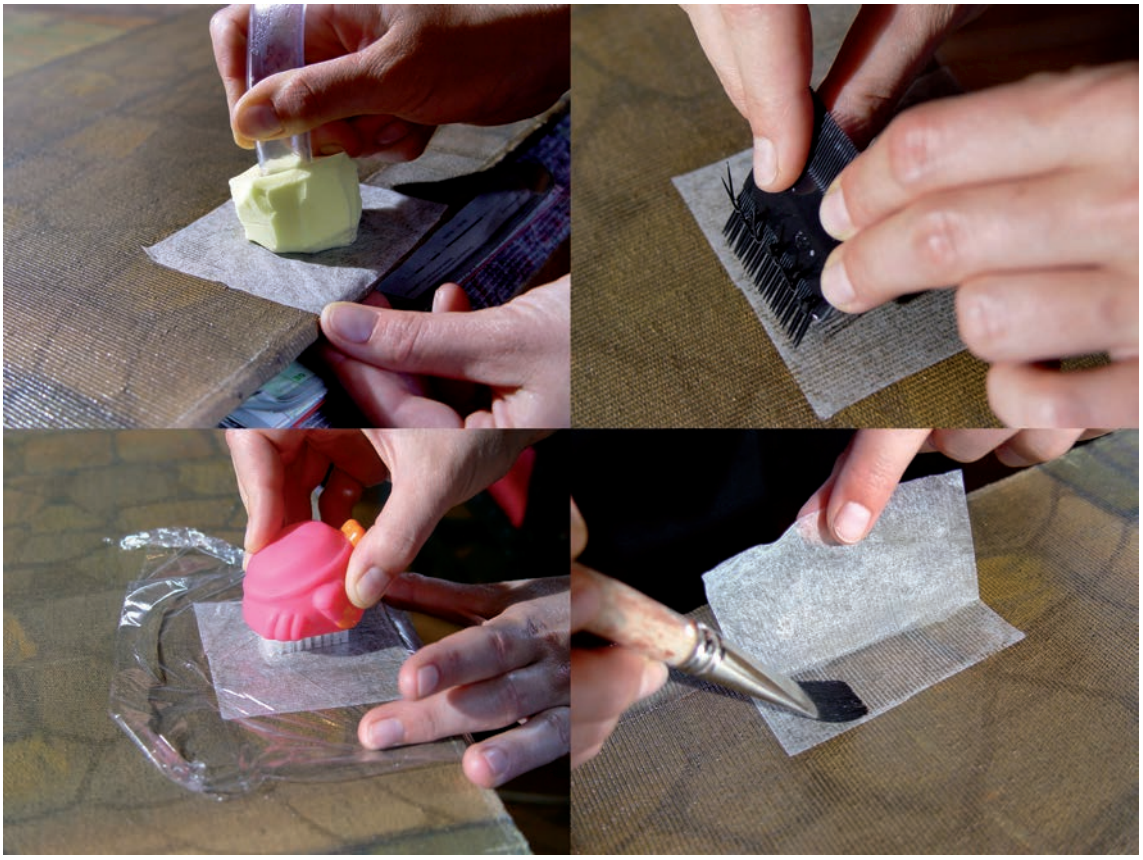


FIGURE 3. Removal of the PVAc varnish in four steps: (top left) Vacuuming the soluble PVAc and acetone through Japanese paper with the Schlürfer. (top right) Pressing down the Japanese paper with a special comb. (bottom left) Strappo technique: applying and peeling off cling wrap with the swollen PVAc material. (bottom right) Removing the PVAc-impregnated Japanese paper with acetone.

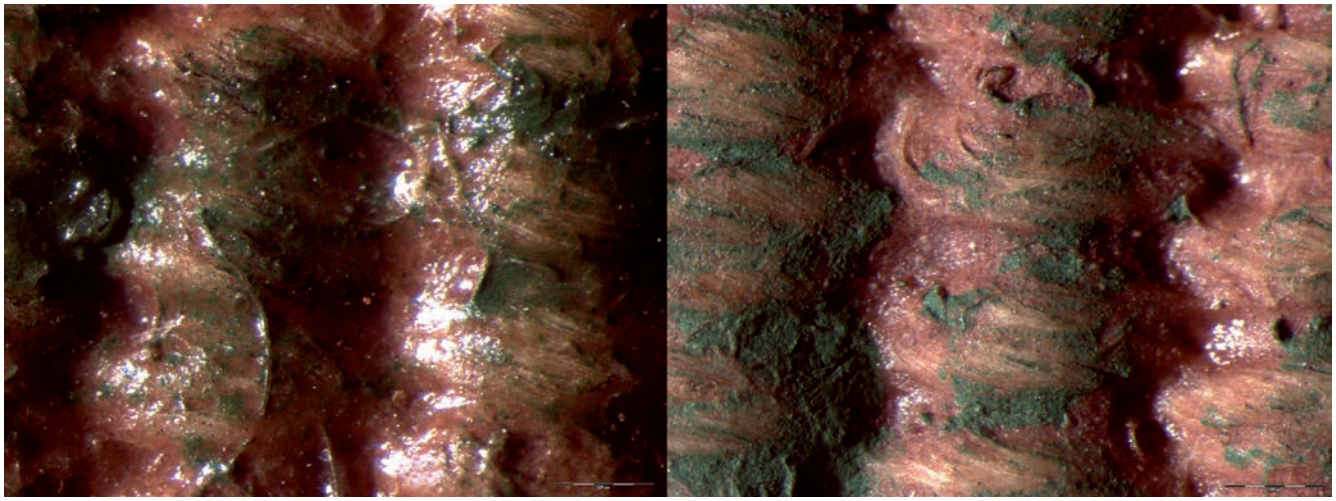


FIGURE 4. Detail of the surface appearance (left) before and (right) after PVAc removal.

of the residual PVAc material in the deep pores of the paint surface and in groove-like depressions of the rib weave were observed, as was the case for the other solvent treatments tested. Further information about this intervention is given elsewhere (Hausmann, 2005).

Acknowledgments

The authors thank Winfried Heiber (deceased 2009) for his brilliant ideas and developments in the field of conservation.

REFERENCES

Hausmann, I. 2005. Removal of an Aged Polyvinylacetat-Varnish on the Painting Ensemble of the Town Council Hall in Buxtehude. Diploma thesis, Cologne University of Applied Sciences, Cologne, Germany.

Nicolaus, K. 1998. *Handbuch der Gemälderestaurierung*. [Manual for Paintings Restoration.] Cologne, Germany: Könemann Verlag.

Extended Abstract—Surface Cleaning with Aqueous Foams

Anne Heckenbücker and Petra Demuth

INTRODUCTION

Several different materials and methods are used for cleaning and removing dirt from paintings in the field of conservation. So far, limited scientific investigations have been conducted on foam cleaning technology (Timár-Balázsy and Eastop, 1998; Gneisinger and Watkinson, 2000) because of little interest. This study presents the first fundamental investigations on the use of aqueous, surfactant-containing foams as a method for cleaning painting surfaces (Heckenbücker, 2009).

The primary aim of the study was to determine the extent to which foams are able to reduce the penetration of cleaning solutions into substrates. Another aspect was to reduce mechanical stress to the surface during the cleaning process. A further objective was to diminish the amount of surfactants required to avoid unwanted residues. Water-based foams were compared to common cleaning methods such as cotton swabs and solvent gels. First of all, a search for appropriate formulations that would result in durable foams was carried out since they do not exist on the market.

THE NATURE OF FOAM

Foam is a two-phase system consisting of a liquid and a gas phase that generally tends to separate into its two phases. Therefore, it is a thermodynamically unstable system. Under the influence of gravitational forces the liquid drains out of foam (Weaire and Hutzler, 1999). It was necessary to find foams that have, on the one hand, a high long-term stability and, on the other hand, a slow, predictable release of the liquid phase. Without these properties, foams are useless for conservators.

The formation of more stable foam structures is ensured by foaming agents. These are surface-active materials that reduce the surface tension of the liquid. The surfactants are found among the most important and successful foaming agents.

MATERIALS AND METHODS

Using characteristic properties such as foaming power, drainage, and the stability of the foam structure, three anionic and two nonionic surfactants, as well as additional

***Anne Heckenbücker**, Weselerstrasse 1, 50733 Cologne, Germany. **Petra Demuth**, Cologne Institute of Conservation Sciences, Cologne University of Applied Sciences, Ubierring 40, 50678 Cologne, Germany. Correspondence: Anne Heckenbücker, anne.heckenbuecker@gmx.de; Petra Demuth, petra.demuth@fh-koeln.de.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

TABLE 1. Tested surfactants and polymers for foam and gel formulations.

Ionic class	Chemical name	Product name	Manufacturer
Nonionic	Fatty alcohol ethoxylate	Marlipal 618/25	Sasol
Nonionic	Polyethoxysorbitan	Tween 20	ICI
Nonionic	Alkyl polyglucoside	Plantacare 818 UP	Cognis
Anionic	Sodium dodecyl-sulfate	SDS	ROTH
Anionic	Fatty alcohol ether sulfate	Texapon NSO	Cognis
Nonionic	Hydroxypropyl cellulose	Klucel H	Hercules
Nonionic	Methylcellulose	Methocel A40M	DOW
Nonionic	Methylcellulose	Methocel A40M	DOW

foam stabilizing polymers (in this study cellulose ether; see Table 1), were tested at different concentrations to find the optimal formulations for the foam generation. The maximum concentration of surfactant and additive was 0.5%. Metrological analyses of currently used and new surfactants alone and also in combination with cellulose ether were carried out. The foam was produced in a foam-generating apparatus with a rotating stirrer.

For further investigations on the interactions between the foam and a surface, the two most stable foams with the lowest rate of draining were selected. One was the pure surfactant Plantacare 818 UP based foam (age: 20 minutes), and the other was Plantacare 818 UP with Methocel A40M as an additive (age: 5 minutes). The penetration depth and spreading of the liquid of the two foams, cotton swab applied, and one water-based methylcellulose gel, 2.5% Methocel A40M (Dow), were metrologically recorded. For this purpose the water phase was dyed with Fuchsin S 1%. Figure 1 shows the different penetration depths of a Fuchsin-dyed solution into an inorganic substrate, gypsum, after a 10 s application with a cotton swab, a Plantacare 818 UP 2 g/L foam, and a water-based methylcellulose gel, 2.5% Methocel A40M.

In order to test the cleaning performance, an alkyd-based paint layer, Winsor & Newton Griffin Alkyd light cadmium yellow, was artificially contaminated with spray-applied dirt. This standardized dirt was a combination of the "special carpet dirt 09 Z" by wfk-Testgewebe GmbH (according to ISO 11378-1 B 2) and a recipe by Wolbers (1992). The cleaning effect was monitored by color measurements using a spectrophotometer (1976 CIE L*a*b* color space following the German Standard DIN 6174).

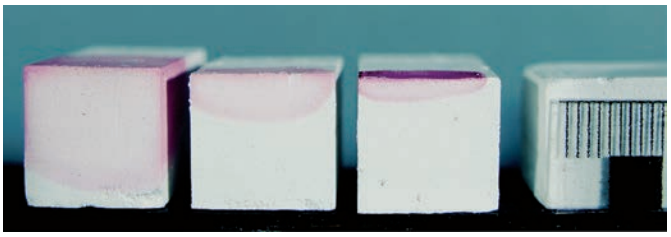


FIGURE 1. Evaluation of the penetration depth of a solution into a substrate. The penetration depth is shown after a 10 s treatment with (left) a cotton swab, (middle) Plantacare 818 UP 2 g/L foam, and (right) water-based methylcellulose gel, 2.5% Methocel A40M. The cube sides measure about 12.5 mm in length.

SUMMARIZED RESULTS

According to the experimental results, the required properties, such as high foam stability and low drainage, seem to be limited to polyhedral foams only. These are defined as foams where the bubbles form polygonal cells, which require an air volume fraction of more than 74% (Stark, 1999:24). A further important observation was that all surfactant-based foams without additives did tend to lose a lot of their liquid phase during the first few minutes (Figure 2). An application of these foams on a painting surface would be acceptable only after a certain waiting period.

The test results show that the use of foam can help minimize the draining and migrating of fluids compared to the use of a cotton swab (Table 2). The tested foams, however, release more water than the tested gel.

It became evident that foams have a general cleaning effect that is similar to the traditional cleaning methods. The cleaning effect was evaluated by color measurements using a spectrophotometer (GRETAG SPM 100, Lab color space CIE 1976 to DIN 6174), and the results are reported in Table 3. The foam system containing alkyl polyglucoside and cellulose ether, compared to that of pure surfactant and to the other methods, led to the best cleaning results if sufficient exposure time was used for its application.

Cleaning with foams has great potential as an alternative to current cleaning methods. An additional benefit is the reduction of mechanical stress during foam removal by vacuuming. Further research on the foam materials for stable foams and a further

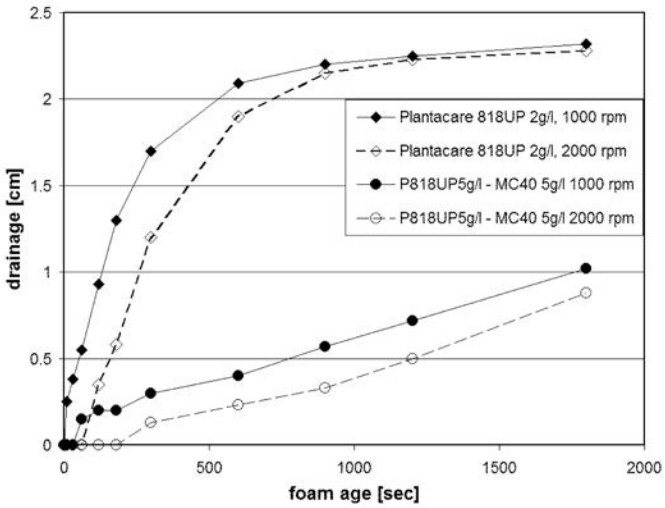


FIGURE 2. Water drainage from freshly prepared foam as a function of age. The impact of different stirring rates during foam generation (open and solid symbols) and different formulations (circles and diamonds) is shown.

TABLE 2. Maximum penetration depth of solution after 10 and 30 s.

Application method	Penetration depths (mm) t = 10 s	t = 30 s
Cotton swab, water	11.97	12.60
Gel, Methocel A40M, 2.5%	2.08	2.23
Gel, Methocel A40M, 2.5%, and rinsing off with water	4.36	5.00
Foam, Plantacare 818 UP 2g/L	4.45	4.65
Foam, Plantacare 818 UP 2g/L, and rinsing off with water	9.21	9.61
Foam, Plantacare 818 UP and Methocel A40M 5g/(5g/L)	6.70	6.78
Foam, Plantacare 818 UP and Methocel A40M 5g/(5g/L) and rinsing off with water	6.69	7.36

reduction of the drainage would be of general interest. This also includes research into the chemical interactions with the surface, decomposition, and aging characteristics of surfactants and foam. Future aims include the transfer of the foam cleaning method from the laboratory into conservation practice as well as the development of a viable technique for foam production.

TABLE 3. Cleaning performance for different formulations and treatment methods evaluated by color measurements. A performance of 100% indicates complete removal of dirt.

Application method	Application Time (s)	Cleaning performance (%)
Cotton swab, water	10	65
Cotton swab, water	30	74
Gel, Methocel A40M, 2.5%	10	73
Gel, Methocel A40M, 2.5%	30	73
Foam, Plantacare 818 UP 2g/L	10	65
Foam, Plantacare 818 UP 2g/L	30	66
Foam, Plantacare 818 UP 2g/L, and rinsing off with water	10	70
Foam, Plantacare 818 UP 2g/L, and rinsing off with water	30	75
Foam, Plantacare 818 UP and Methocel A40M 5g/(5g/L)	10	71
Foam, Plantacare 818 UP and Methocel A40M 5g/(5g/L)	30	76

Acknowledgments

The authors gratefully acknowledge Cognis GmbH Company, Duesseldorf (Germany), for the surfactants and the use of the foam-generating apparatus. The authors give special thanks to Matthias Hloucha for his expert opinion and professional collaboration and thank wfk-Testgewebe GmbH for their help by producing the artificially standardized dirt.

REFERENCES

Gneisinger, W., and D. Watkinson. 2000. "Innovative Uses for Aqueous Foams in Conservation Practice." In *Tradition and Innovation Advances in Conservation: Contributions to the Melbourne IIC Congress,* ed. A. Roy and P. Smith, pp. 77–81. London: The International Institute for Conservation of Historic and Artistic Works.

Heckenbücker, A. 2009. Oberflächenreinigung mit wässrigen Schäumen. [Surface Cleaning with Aqueous Foams.] Master's thesis, Cologne Institute of Conservation Sciences, University of Applied Sciences, Cologne, Germany.

Stark, K. 1999. Rheologische Eigenschaften von Schäumen und deren Beeinflussung unter Berücksichtigung der Schaumstabilität. [Rheological Properties of Foams and Their Interference Considering Foam Stability.] Ph.D. Diss., University of Bayreuth, Bayreuth, Germany.

Timár-Balázsy, Á., and D. Eastop. 1998. *Chemical Principles of Textile Conservation*. Oxford: Butterworth-Heinemann.

Weaire, D., and S. Hutzler. 1999. *The Physics of Foams*. Oxford: Clarendon Press.

Wolbers, R. 1992. The Use of a Synthetic Soiling Mixture as a Means for Evaluation the Efficacy of Aqueous Cleaning Materials on Painted Surfaces. *Conservation et restauration des biens culturels,* 4:22–29.

Extended Abstract—Residues on Unvarnished Surfaces after Absorene Sponge Dry Cleaning

Shawn Digney-Peer and Julie Arslanoglu

INTRODUCTION

The accumulation of surface dirt, most commonly deposited through airborne pollutants, is a concern that affects all paintings that are not displayed or stored in glazed and sealed microclimates. A common conservation treatment involves the removal of this deposit, which alters the aesthetic quality of a work of art by shifting contrast and color values of the paint film (Eastaugh, 1990).

Surface cleaning is usually straightforward for paintings that have intact varnish layers, as the coatings protect the paint films and may facilitate the removal of dirt layers. However, removing surface grime from unvarnished artwork is often problematic as unvarnished paint films are frequently sensitive to solvent and aqueous cleaning methods (Perry, 1990; Mills et al., 2008; Ormsby and Learner, 2009). In such instances it is common to attempt dry cleaning techniques, although these also pose risks. Unvarnished paintings may be damaged by mechanical action produced by the manipulation of the cleaning material against the paint surface. Damage may involve abrasion, changes in gloss, dislodgement of pigment from underbound paint, or even future changes resulting from the aging of residues deposited by the cleaning material (Paerlstein et al., 1982; Estabrook, 1989; Sterlini, 1995; Brokerhof et al., 2002; van den Berg et al., 2008). This study examines the potential for residue deposition from Absorene sponges when they are used for dry surface cleaning.

EXPERIMENT

Absorene Dry Cleaning Soot Sponges (as opposed to Absorene Paper and Book Cleaner, which is a different material) are commercial natural rubber sponges that were selected for this study because of their frequent use on unvarnished modern and contemporary paintings. These paintings often incorporate materials such as raw canvas, exposed ground, paint, and paper.

Initial characterization of the sponge using attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR) showed that the spectrum of the bulk material is consistent with that of natural rubber, with the addition of calcium carbonate. When the sponge was compressed and then released in the FTIR diamond cell holder, a residue was deposited on the diamond surface as the sponge contracted (Figure 1).

***Shawn Digney-Peer**, Sherman Fairchild Paintings Conservation Center, The Metropolitan Museum of Art, 1000 Fifth Avenue, New York, New York, 10028-0198, USA. **Julie Arslanoglu**, Department of Scientific Research, The Metropolitan Museum of Art, 1000 Fifth Avenue, New York, New York, 10028-0198, USA. Correspondence: Shawn Digney-Peer, shawn.digney-peer@metmuseum.org.;JulieArslanoglu,julie.arslanoglu@metmuseum.org.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

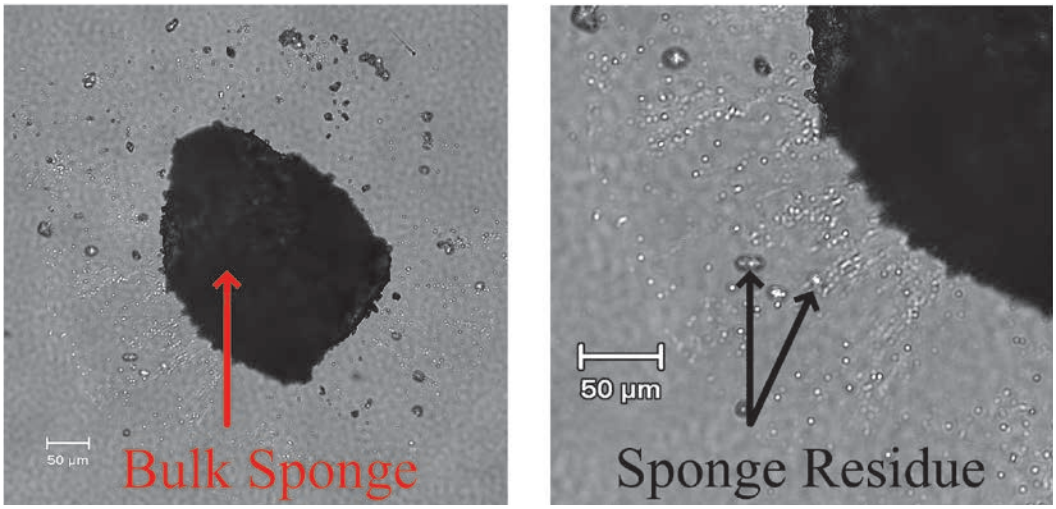


FIGURE 1. (left) Photomicrograph of the FTIR diamond compression cell containing a sample of the bulk sponge and (right) a detail of the sponge residue.

This residue exhibited an FTIR spectrum that was not chemically identical to the bulk sponge, but rather was more similar to an alkane material.

The sponge was further characterized by obtaining a thermal profile using evolved gas analysis (EGA). The EGA profile reveals the components in the sponge that are desorbed or pyrolyzed as the temperature is increased. Three distinct regions were exhibited for the Absorbene sponge (Figure 2, inset). The first region is composed of volatile and semivolatile materials, which can be isolated using thermal desorption–gas chromatography–mass spectrometry (TD-GC-MS) and was identified as containing long-chain aliphatic hydrocarbons. This is the material that is referred to here as the residue. The second region is a polymeric material, which was analyzed by pyrolysis-GC-MS (Py-GC-MS) and was identified as natural rubber (isoprene). The third region indicates nonvolatile materials, and a mass spectrum of this region revealed the presence of carbon dioxide, which indicates the pyrolysis of calcium carbonate, a component of the Absorene sponge identified using FTIR.

The use of TD-Py-GC-MS on Absorene sponges confirmed that natural rubber (isoprene) is the main component of these sponges as well as a fraction of semivolatile aliphatic hydrocarbons present (Figure 2). In this technique, the volatile and semivolatile components from a sample were thermally desorbed at lower temperatures (between 55°C and 250°C) than used in pyrolysis, thus leaving the bulk of the polymerized and less volatile

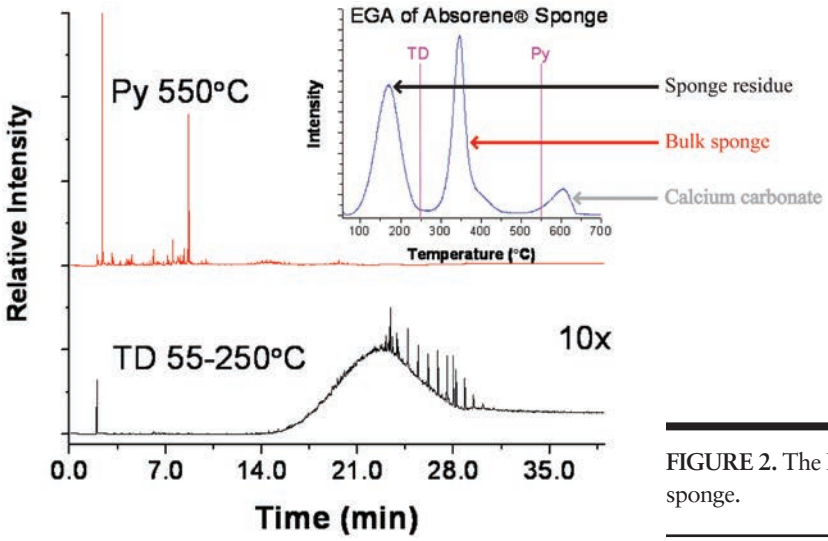


FIGURE 2. The EGA and TD-Py-GC-MS characterization of the Absorene sponge.

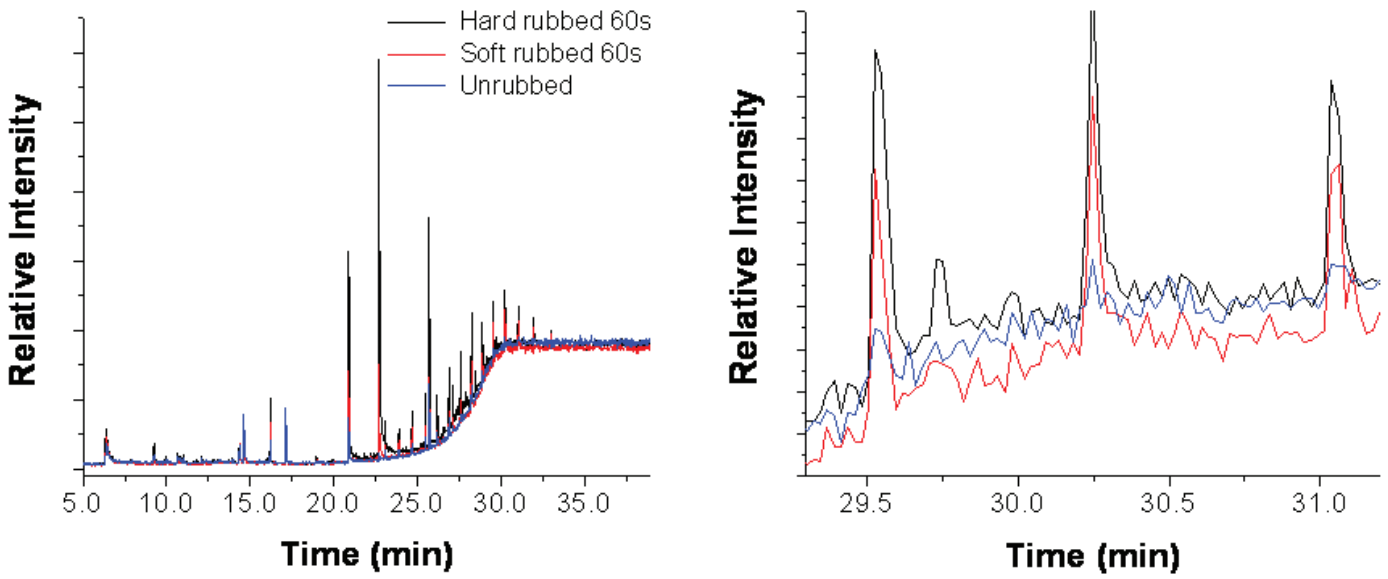


FIGURE 3. The effect of rubbing pressure on the occurrence of deposition on seventeenth-century paper: (left) TD-GC-MS chromatogram of rubbed (soft and hard) and unrubbed paper; (right) detail of the region of the chromatogram showing the presence of alkane residue (note that no residue is visible on the unrubbed paper, as corroborated by MS data).

components unchanged. The Py-GC-MS was then performed on the remaining material. Most importantly, TD-GC-MS allowed the separation and analysis of components of the sample that generally would be lost in the multitude of peaks generated in a typical pyrogram because of their low concentration and, in general, lower molecular weight.

Test samples of paper of various textures, cotton duck, primed cotton duck, and painted cotton duck were prepared. These samples were then rubbed with Absorene sponges. The amount of pressure and rubbing time was varied in order to establish under what conditions, if any, residue deposition could occur. Rubbing duration and pressure was carried out at potential treatment levels and at longer and harder levels than normal treatment would generally involve (5, 20, 30, and 60 s at soft and hard pressure) in order to establish if residue deposition could be detected. All samples were brushed in order to remove loose particulate matter deposited by the sponge and then were examined under the microscope before analysis.

DISCUSSION AND CONCLUSIONS

This preliminary study shows that the aliphatic hydrocarbon material may be retained on some substrates when Absorene sponges are used to remove surface deposits. The results showed that with an increase in time and/or pressure there was an increase in deposition of the material on all surfaces tested (Figure 3). The rougher, more absorbent surfaces seemed to have more deposition than the smoother surfaces. Since Py-GC-MS of some of the samples with the most deposition did not show the presence of isoprene, it appears that the aliphatic hydrocarbons detected by TD-GC-MS are not produced from microscopic particles of the sponge. An investigation of potential submicroscopic particles is ongoing.

Although aliphatic hydrocarbons are essentially unreactive, their presence as residues could potentially change the chemical properties of a surface. This could result in increased hydrophobicity, which, along with changes in surface roughness, could affect the attraction potential of the surface for airborne grime. The amount of residue appears to decrease with decreasing pressure and duration of sponge application. Rougher, more absorbent surfaces (unprimed cotton duck and paper) exhibited greater residue deposition than smoother, less absorbent surfaces (primed cotton duck and paint). Deposition, therefore, may be contingent on characteristics of surface roughness and/or absorbency. Further research is required to increase our understanding of these phenomenona.

REFERENCES

Brokerhof, W., S. de Groot, J. Luiz Perdesoli Jr., H. van Keulen, B. Reissland, and F. Ligterink. 2002. Dry Cleaning, the Effect of New Wishabs Spezialschwamm and Spezialpulver on Paper. *Papier Restaurierung*, 3(2):13–19.

Eastaugh, N., 1990. "The Visual Effects of Dirt on Paintings." In *Dirt and Pictures Separated*, ed. V. Todd, pp. 19–23. London: United Kingdom Institute for Conservation of Historic and Artistic Works.

Estabrook, E., 1989. Considerations of the Effect of Erasers on Cotton Fabric. *Journal of the American Institute for Conservation*, 28: 79–96. http://dx.doi.org/10.2307/3179482.

Mills, L., A. Burnstock, S. de Groot, L. Megens, M. Bisschoff, H. van Keulen, F. Duarte, and K. J. van den Berg. 2008. "Water Sensitivity of Modern Artists' Oil Paints." In *Preprints ICOM-CC 15th Triennial Conference, New Delhi*, Volume 2, ed. J. Bridgland, pp. 651–659. New Delhi: Allied Publishers.

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.

Pearlstein, E. J., D. Cabelli, A. King, and N. Indictor. 1982. Effects of Eraser Treatment on Paper. *Journal of the American Institute for Conservation,* 22(1):1–12. http://dx.doi.org/10.2307/3179714.

Perry, R., 1990. "Problems of Dirt Accumulation and Its Removal from Unvarnished Paintings: A Practical Review." In *Dirt and Pictures Separated*, ed. V. Todd, pp. 3–6. London: United Kingdom Institute for Conservation of Historic and Artistic Works.

Sterlini, P., 1995. Surface Cleaning Products and Their Effects on Paper. *Paper Conservation News,* 76:3–7.

van den Berg, K. J., M. Daudin, I. Joosten, B. Wei, R. Morrison, and A. Burnstock. 2008. A Comparison of Light Microscopy Techniques with Scanning Electron Microscopy for Imaging the Surface Cleaning of Paintings. Paper presented at 9th International Conference on NDT of Art, Jerusalem. http://www.ndt.net/search/docs.php3?MainSource=65 (accessed 28 November 2012).

Extended Abstract—The Use of Ionic Liquids for Varnish Removal: Effectiveness and Risk Evaluation

Maria Filipa Pacheco, Ana I. Pereira, A. Jorge Parola, and Luís C. Branco

INTRODUCTION

The development of less harmful cleaning methods, both for health and the environment, is one of the major concerns for conservators and restorers (McCann, 1992). Therefore, the possibility of replacing volatile and toxic organic solvents by ionic liquids (ILs) could contribute to safer procedures. Ionic liquids can be defined as organic salts with melting points below 100°C, constituted by an organic cation and an inorganic or organic anion. Some of the properties of ILs (Branco et al., 2002; Rogers and Seddon, 2002; Wilkes, 2002; Poole, 2004; Dupont, 2005) can be useful for the conservation of paintings. For example, their low volatility reduces the risks to health and the environment, their high viscosity may inhibit the penetration into the pictorial layers, and their adjustable miscibility with water or less toxic solvents (e.g., alcohols) allows their removal with safer solvents. This study evaluated the effects and consequences of possible cleaning operations with ILs. The effectiveness and risk evaluation was carried out through the application of different types of ILs in mock-ups prepared with various painting materials and varnishes.

MATERIALS AND METHODS

The samples aimed to mimic real cases in oil paintings. To assess the role of the colorants, the colors used in the test systems were selected on the basis of the predicted pigment effect on oil drying and aging. For example, lead white acts as a drier and promotes the reticulation of the polymer, which makes the paint less vulnerable to solvents, whereas red lake and Vandyke brown are slower driers (Carlyle, 2001) that inhibit drying of the oil and make the paint layer more sensitive to the effect of the cleaning products. Three different varnishes were applied over three sections of a 17-year-old oil paint sample, half with lead white and half with Vandyke brown. The three varnishes were a natural resin (dammar) and two synthetic varnishes, polyvinyl acetate (PVAc) and cyclohexanone resin (Retouching Varnish, Talens).

To reproduce the materials and techniques found in modern and contemporary art, a painting mock-up was prepared with an acrylic medium, poly(*n*-butyl acrylate-methyl

***Maria Filipa Pacheco**, Departamento de Conservação e Restauro, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal. **Ana I. Pereira**, Departamento de Conservação e Restauro, FCT, and REQUIMTE, CQFB, Departamento de Química, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal. **A. Jorge Parola** and **Luís C. Branco**, REQUIMTE, CQFB, Departamento de Química, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal. Correspondence: Maria Filipa Pacheco, maria filipa.pacheco@gmail.com; Ana Isabel Pereira, ana.pereira@campus.fct.unl.pt; A. Jorge Parola, ajp@fct.unl.pt; and Luís C. Branco, l.branco@fct.unl.pt.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

methacrylate) (Rembrandt Acrylic Colours, Talens), and coated with an acrylic varnish, poly(isobutyl methacrylate) (Acrylic Varnish Matt, Talens). The varnish was applied 1 month after the application of the acrylic paint and left to dry for approximately 1 month before cleaning tests were carried out.

The ILs were chosen according to the polarity of the liquid itself and the nature of the paint layers and varnishes to be removed. A total of 13 commercial ILs were tested (Aldrich, Solchemar). The cleaning tests were performed under a stereomicroscope (Olympus SZx12) in three steps: (1) application of the IL to the surface, (2) after 10 minutes, removal with a dry swab, and (3) rinsing with a water-wetted swab.

Images of the surface were obtained with an optical microscope (Axioplan 2) that provides information about varnish removal effectiveness. This method was also used to examine paint cross sections. The results were assessed by Fourier transform infrared microspectroscopy (FTIR; Nexus and Continuum-Nicolet) in the transmitted and attenuated total reflection (ATR) modes. These analytical methods allowed verification of complete varnish removal and detection of eventual IL residues left on the surface.

RESULTS AND CONCLUSIONS

The following ILs did not prove to be effective: [C_2OHmim][BF_4], [C_5O_2mim][Cl], [emim][$EtSO_4$], [emim][MOEOEtSO_4], [$P_{6,6,6,14}$][Cl], and [choline][Ac]. None of these ionic liquids were efficient in the removal of the Acrylic Varnish Matt, and therefore, the mimicked modern paints were not examined further in this study. The ILs that proved to be effective in the cleaning tests are listed in Table 1, where the results obtained are also summarized.

In Figure 1 the removal of PVAc varnish with [bmim][BF_4] as characterized by optical microscopy and FTIR-ATR is shown. In this particular case, the IL was removed with a swab embedded in water, but in the cases of the Aliquat ILs, water and

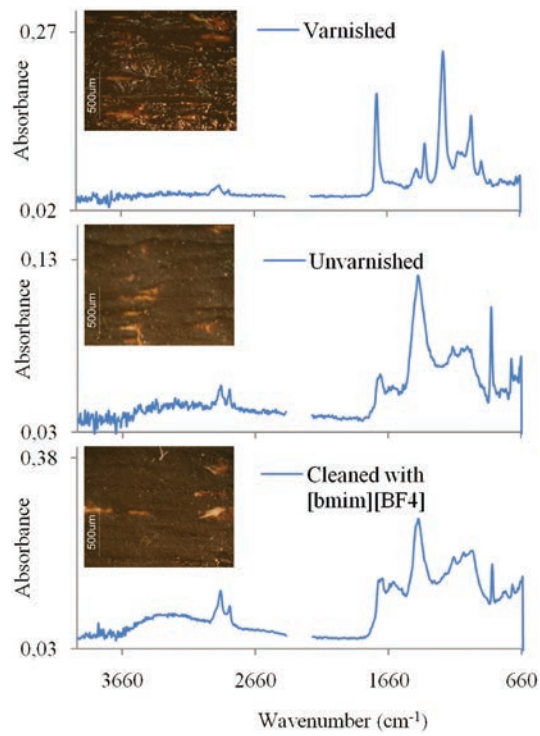
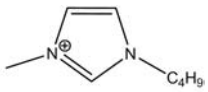
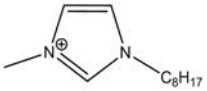
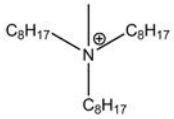


FIGURE 1. Optical microscope images and FTIR-ATR spectra during the removal of the PVAc varnish from oil paint with [bmim][BF_4].

TABLE 1. Results of effective varnish removal from over oil paint with several ionic liquids. M = more effective removal; L = less effective removal.

Ionic liquids	Cation	Anion	Dammar	Retouching varnish	PVAc Varnish
[bmim][DCA]		NC——N⊖——CN	M	M	M
[bmim][BF_4]		$BF_4^{\ominus}$			M
[bmim][TfO]		$CF_3SO_3^{\ominus}$			L
[bmim][TFA]		$CF_3COO^{\ominus}$			L
[omim][Cl]		$Cl^{\ominus}$	M	M	
[Aliquat®][DCA]		NC——N⊖——CN	L	M	
[Aliquat®][Cl]		$Cl^{\ominus}$		M	

ethanol mixtures were required because of the low solubility of these ILs in water.

One important issue to consider is the presence of IL residues left by the cleaning procedure. The FTIR-ATR was useful for detecting ILs with specific signals, such as those containing dicyanamide (DCA) (CN stretching at 2160 cm^{-1}; Hummel, 2002). For example, when cleaning the dammar varnish with [bmim][DCA], IR signals of DCA could be detected in some points. Other techniques such as spectrofluorimetry are being exploited to further reveal the presence of residues.

The results presented suggest the potential of ILs as cleaning agents for varnish removal in paintings. For each varnish it was possible to identify at least one IL that efficiently removed it.

Acknowledgments

The authors thank Leslie Carlyle for providing one of the mock-ups used.

REFERENCES

Branco, L. C., J. N. Rosa, J. J. M. Ramos, and C. A. M. Afonso. 2002. "Preparation and Characterization of New Room Temperature Ionic Liquids." in *Chemistry—A European Journal,* 8(16):3671–3677. http://dx.doi.org/10.1002/1521-3765(20020816)8:16<3671::AID-CHEM3671>3.0.CO;2-9.

Carlyle, L. 2001. *The Artist's Assistant*. London: Archetype Publications.

Dupont, J. 2005. "Ionic Liquids: Structure, Properties and Major Applications in Extraction/Reaction Techonology." In *Green Separation Processes: Fundamentals and Applications,* ed. C. A. M. Afonso and J. P. G. Crespo, pp. 229–245. New York: John Wiley.

Hummel, D. 2002. *Atlas of Plastic Additives*. New York: Springer.

McCann, M. 1992. *Artist Beware*, Guilford, Conn.: The Lyons Press.

Poole, C. F. 2004. Chromatographic and spectroscopic methods for the determination of solvent properties of room temperature ionic liquids. *Journal of Chromatography A,* 1037:49–82. http://dx.doi.org/10.1016/j.chroma.2003.10.127.

Rogers, R., and K. R. Seddon. 2002. *Ionic Liquids: Industrial Applications for Green Chemistry*. Washington, D.C.: American Chemical Society.

Wilkes, J. S. 2002. A Short History of Ionic Liquids—From Molten Salts to Neoteric Solvents. *Green Chemistry,* 4:73–80. http://dx.doi.org/10.1039/b110838g.

Extended Abstract—Laser Cleaning Applied to Contemporary Paintings: Optimization of Working Parameters

Grazia De Cesare, K. Melessanaki, P. Pouli, J. Domingues, F. Rosi, C. Miliani, and C. Fotakis

INTRODUCTION

Twentieth-century paintings made with industrial paints have often been restored without a thorough knowledge of their chemical and physical properties (Learner, 2004). In particular, contemporary paintings have often been retouched using materials rather similar to the originals, thus compromising the actual reversibility of the overpainting. Therefore, the selective removal of overpaints is a challenging task in these cases (Melessanaki et al., 2006) as the use of organic solvents may often be limited because of their lack of selectivity (Bordalo et al., 2006; Ormsby and Smithen, 2006–2009). Lasers may offer a viable solution for the selective removal of overpaints without compromising the underlying original layers (Fotakis et al., 2006).

LASER CLEANING TESTING

To test both effectiveness and limitations of laser cleaning in contemporary paintings, an integrated study was carried out on painting mock-ups, which were irradiated with different laser parameters (wavelength, energy density, number of pulses, etc.) and then analyzed by optical microscopy, micro–Fourier transform infrared spectroscopy (FTIR), and micro–Raman spectroscopy.

Six mock-ups (cotton canvases on stretchers) were prepared by respectively applying six different binders (commercial tube formulations) with titanium white. Then a second layer was applied on each of the six canvases. This second layer was applied in 11 squares, leaving 1 square of the first layer exposed. Five of the 11 squares were the other five commercial binders with titanium white. Six squares were with the six commercial tube formulations with either ultramarine blue or phthalocyanine blue. The binders used were acrylic emulsion resin (for artists), vinyl emulsion resin (for artists), acrylic in solvent, oil-modified alkyd (for artists), oil-modified alkyd (household), and alkyd with nitrocellulose (for artists). For the blue paints, the ones for artists contained ultramarine blue, whereas the others (acrylic in solvent and household oil-modified alkyd) contained phthalocyanine blue.

***Grazia De Cesare**, Area di Restauro dei materiali contemporanei, Istituto Superiore per la conservazione ed il restauro, Via di San Michele 23, 00153 Rome, Italy. **K. Melessanaki**, **P. Pouli**, and **C. Fotakis**, Institute of Electronic Structure and Lasers, Foundation of Research and Technology, P.O. Box 1385, 71110 Heraklion, Crete, Greece. **J. Domingues** and **F. Rosi**, Scientific Methodologies Applied to Archaeology and Art, Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy. **C. Miliani**, Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy, and CNR-ISTM, Via Elce di Sotto 8, 06123 Perugia, Italy. Correspondence: Grazia De Cesare, grazia.decesare.icr@beniculturali.it.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

The cleaning procedures tested were based on different laser systems with wavelengths ranging from the ultraviolet (248 nm) up to near infrared (1064 nm), with various pulse lengths t_p. In all cases the objective was to remove the outer layer without affecting the white ground layer. Preliminary cleaning tests were performed mainly on a spot basis in order to define the optimum parameters for effective and safe removal of the overpaint and to establish the limitations of this method. This was followed by scanning tests in order to develop the appropriate cleaning methodology.

The effectiveness of laser cleaning to remove the outer layer without affecting the ground paint was evaluated using different physical and spectrophotometric tools. In particular, optical microscopy, micro-FTIR, and micro–Raman spectroscopy were employed to evaluate the irradiation tests (cleaning efficiency, color homogeneity, and surface morphology; De Cesare et al., 2008) and to perform a chemical analysis of the irradiated surfaces, whereas laser-induced fluorescence was used to monitor the cleaning process.

RESULTS

A very strong gray discoloration was evident on titanium white paint upon irradiation for all the laser parameters tested, even using single-pulse irradiation at very low energy densities. Still, no laser-induced discoloration (which is a well-known issue in laser cleaning applications) was observed on the blue paints. Using the UV wavelengths, it was possible to remove the unwanted overlayers in a stratigraphic (layer by layer) manner.

The most efficient cleaning results in our tests were obtained using the 355 nm laser in the nanosecond range at rather high energy densities and several pulses (~10). On the other hand, the KrF Excimer emitting at 248 nm (t_p = 30 ns) required higher flux values and a significant number of pulses in order to produce an efficient cleaning level (flux [F] > 3 J/cm^2 and 10–50 pulses).

The Nd:YAG laser was not very satisfactory at either 532 or 1064 nm (10 ns). In particular, the 532 nm wavelength did not result in a good cleaning level except in certain areas, and even in those cases the removal was never homogeneous, mainly because of the inhomogeneities of the beam profile. Similarly, IR radiation at 1064 nm had an apparent abrasive effect without any control. Furthermore, strong photochemical effects (visible as crack formation around the irradiation craters) were recorded.

Parallel tests were performed to investigate the conditions that would eliminate the white ground with minimal disruption to the canvas (i.e., without discoloration and damage to the fibers). The best results were obtained on the white alkyd ground using the 355 nm (t_p = 150 ps, F = 1.4 J/cm^2, and 20 pulses). The spectrophotometric analysis of the irradiated surfaces by micro-FTIR and micro-Raman spectroscopy revealed residues of the outer-layer materials as well as the presence of alteration phases responsible for color changes.

DISCUSSION AND CONCLUSIONS

A systematic study, integrated with the physical and chemical analysis of the paints, confirmed that ultraviolet wavelengths (at 248 nm and, in certain cases, at 355 nm) were the most appropriate ones for an effective and safe removal of unwanted retouches on contemporary paintings. Tests with IR laser radiation (at 1064 nm) were found to be particularly aggressive, resulting mostly in ground damage but also inducing photomechanical effects visible as cracks around the irradiation craters and with a limited selectivity option. On the other hand, the visible radiation (at 532 nm) could not reach an acceptable cleaning level at the tested energies, and further studies are being conducted in this regime in order to exploit all the possibilities (i.e., lower fluxes).

The discoloration phenomena observed upon irradiation of titanium white, which is a strong UV absorber and a redox catalyst, could be related to traces of carbon detected on the irradiated surfaces, most probably because of the degradation of the organic medium. The removal of white overpaints appears to be far more demanding than the blue ones, which generally were removed more easily and effectively. An important issue that should also be addressed when developing the cleaning methodology is the appearance of a dark "halo" that was visible around the irradiation spots and was attributed to redeposition of alteration products upon laser ablation. The fine-tuning of the operational parameters toward the development of the optimum laser cleaning methodology for every individual material tested is currently being researched.

REFERENCES

Bordalo, R., P. J. Morais, H. Gouveia, and C. Young. 2006. Laser Cleaning of Easel Paintings: An Overview. *Laser Chemistry,* 2006: 90279. http://dx.doi.org/10.1155/2006/90279.

De Cesare, G., A. Daveri, K. Kahrim, and C. Miliani. 2008. "Monitoring Cleaning Procedures through Non-invasive Measurements: A Case Study." Paper presented at 9th International Conference on NDTof Art, Jerusalem. http://www.ndt.net/article/art2008/papers/133DeCesare.pdf (accessed 14 May 2012).

Fotakis, C., D. Anglos, V. Zafiropulos, S. Georgiou, and V. Tornari. 2006. *Lasers in the Preservation of Cultural Heritage: Principles and Applications*, ed. R. G. W. Brown and E. R. Pike. New York: Taylor and Francis.

Learner, T. J. S. 2004. *Analysis of Modern Paints*. Los Angeles: The Getty Conservation Institute.

Melessanaki, K., C. Stringari, C. Fotakis, and D. Anglos. 2006. Laser Cleaning and Spectroscopy: A Synergistic Approach in the Conservation of a Modern Painting. *Laser Chemistry*, 2006: 42709. http://dx.doi.org/10.1155/2006/42709.

Ormsby, B., and P. Smithen. 2006–2009. Evaluating the Effects of Cleaning Acrylic Paintings—The Tate AXA Art Modern Paints Project. http://www.tate.org.uk/research/tateresearch/majorprojects/conservation_modernpaints.htm (accessed 31 January 2010).

Ending Note: Summary of Panel Discussions

Jacqueline Ridge

A testament to the interest and commitment of the conservation and restoration profession in furthering the understanding of the cleaning of paintings is surely that over 600 delegates not only attended the presentations during the week but also remained to participate in the two-hour panel discussion at the end of the conference. Delegates represented countries from around the world and the full gamut of working environments, from the national institution to private restorer, and the discussions brought together a wide spectrum of views and approaches.

The panel session was the instrument by which the delegates could respond to and debate the threads that had woven themselves through the lectures and poster session presentations. It was the opportunity to bring to the fore those conversations that happened outside the conference auditorium, those conversations that are frequently the true testing ground for an individual's understanding and their drive to shift or change an approach to practical conservation.

The panel comprised Marion Mecklenburg, Museum Conservation Institute, Smithsonian Institution, USA; Alan Phenix, Getty Conservation Institute, USA; Stephen Gritt, National Gallery, Canada; Paolo Cemonesi, Cesmar7, Italy; and Pilar Sedano, Museo del Prado, Spain. Their function was to build on and respond to the debate from the floor.

The level of debate demonstrated a maturity of thinking within the field and the challenges posed by the complexities of balancing science and practice. It included a high level of self-analysis and reflection, and four key questions developed that served to summarize the conclusions that could be drawn.

1. *Why do we clean paintings: Is there ever a situation where aesthetics are the sole reason for choosing to undertake a restoration treatment?*

There was a marked difference in stance around this subject with a strong sense among many that pure aesthetics is frequently the driver for cleaning a painting. As the conversation developed, it was clear that any differences primarily reflected where the conservator sat in the chain of decision making.

It is unquestionably the case that every restoration has a context, but can it simply be based on aesthetics? It is hard to imagine a situation where a restoration takes place without the decision being made because of a bigger context, for example, in readiness for a planned upcoming exhibition, a loan, a potential buyer, or following stabilization of structural problems. Where conservation resources are in excess of demand, it might be

***Jacqueline Ridge**, National Galleries of Scotland, 75 Belford Road, Edinburgh EH4 3DR, UK. Correspondence: jridge@nationalgalleries.org.* *Manuscript received 19 November 2010; accepted 24 August 2012.*

possible to see an aesthetic consideration being the primary driver for a treatment program, but such a situation is surely rare.

From the delegates' response it was evident that the role of the conservator within the decision-making process that decides when a restoration is to be undertaken and varies significantly between nations, between galleries, and within the commercial world. Such variation also underlies the ability of individual conservators to influence and drive change to any approach to cleaning.

2. *Is it desirable to have a standardized framework or methodology for the thinking process for approaching the cleaning of a painting?*

The lectures throughout the week reflected thinking that supported both inward-looking solutions to conservation methods following local political contexts and personal knowledge and outward-looking approaches with conservators as part of an international framework or profession. The debate likewise reflected this range of viewpoints.

Where the point is that will allow differences in approach that are artwork specific to be in balance with similarities in approach that will underpin best practice is difficult to identify. Is it appropriate to have a profession with an international standard to cleaning that at the same time maintains pronounced national approaches to presentation and care or that fundamentally supports a difference between the commercial and noncommercial worlds?

Some delegates felt that a framework for cleaning was a set of rules that would prevent thinking or would provide a fail-safe answer or that would present cleaning solutions that were only viable with dedicated scientific support. It would seem that a standardized framework needs to balance these extremes and that it should provide guidance and direction for best practice, be a system that facilitates thinking and logic of thought, and offer a structure that supports conservators in whichever work environment they practice.

The question as to how far it is possible for the practicing conservator to bridge "the gap" between intuitive cleaning and scientific theory remained and is possibly the biggest barrier to a standardized framework. Our ability to bridge a perceived gap will depend on developing further a shared vocabulary that all can use. It is also essential that the value judgments that are perhaps given to these two approaches need to be removed from the equation. Intuitive cleaning is based on experience and past practice, practice and experience that was developed and underpinned by research and science. They are necessarily iterative in nature.

3. *Is it appropriate to universally ban a cleaning agent?*

Although not a question directly posed by the delegates, it was an undercurrent through many discussions. A simple answer "yes" was the feeling that seemed to be at the core of this question; however, this is surely predicated by the absence of a standardized cleaning "thinking" methodology. With such a methodology in place the banning of materials on grounds other than health and safety becomes less necessary; the thinking process to decide and make choices will be based on an array of factors, including the object, the materials it comprises, how these interact with the materials to be removed, and the aesthetic aim of the endeavor.

4. *Should all conservators retain the right to state a painting is uncleanable?*

The position of the conservator in the decision-making process of "whether to clean a painting or not" was variable. A sense that caution toward cleaning was highly desirable embodied much of the discussions. Similarly, it was very clear that here the view was that cleaning paintings would always take place regardless of any position taken by professional conservation bodies. A moratorium on cleaning therefore becomes self-defeating. The process of considered conservation treatment is the driver for future research and dissemination of information and understanding. Of far greater value, as demonstrated by this conference, is to support the drive and commitment of the profession to discuss, debate, and share research and experience. Individuals retain the right to state a painting is uncleanable within the context of contemporary understanding. In this spirit the challenge remains to ensure that research into cleaning is embedded as fully as possible into all corners of the field.

Index

TABLES in **BOLD;** *Figures* in *Italic*

abrasion
  analysis of surface, *24*, 24–25
  caused by dry cleaning, 214, *215*, *216*
  varnish removal by, 13
Absorene, **210**, **212**, *212*, **213**, 215, *218*, 229–31, *230*, *231*
acetone
  effect on egg tempera, 40
  effect on oil paint, *56*, *57*, **57**, *62*, *64*
  effect on polymeric films, **166**
  effect on polyvinyl acetate (PVAc) paint, 129–30, *130*
acrylic paints
  additives, 132, 159
  components of, 141
  conductivity of cleaning solutions on, 147, 153
  drying of, 141, *142*
  emulsion effects on, *131*, 132–33, *132*, *133*
  gel effects on, *131*, 132–33, *132*, *133*
  history of paintings using, 147–48
  ionic strength of cleaning solutions for, 143–44, *151–52*
  outdoor murals using, 148–49
  pH of cleaning solutions for, 141–42, 153
  pigments and cleaning sensitivity, *127*, 127, *128*, 128, 133, 172, *173*
  solvent effects on, 129–30, *131*, *132*, 136, *137,* 148–49
  surfactants and, 144–45, 149, 151, 153, *154–55*, *160–62*
  swelling of, 127, 130, 132, 133, 143, 149–50, *151–52*, 153
  varnish removal from, 169–73
  water immersion effects on, 127–28, *128*, *129*, *131*, *132*, *133*
  water sensitivity of, *127*, 127, 149
  water swabbing effects on, 128–29, *130*, *132*, *133*, **162**, 162–63, *164*
  See also Modular Cleaning Program (MCP)
agar. *See* rigid gels
agar cyclododecane, 205–7
agarose, 180. *See also* rigid gels
aging
  artificial, 70, 78, 108, *110,* 135, 210
  changes in oil paint from, 46–47
alkyd paint, 89
  advantages of, 89–90
  aging problems of, 92–94
  characterization of, 91–92, *92*
  conservation problems with, 91, *91*, 94

alkyd paint (*continued*)
disadvantages of, 90, 92
influence of pigments on, 62–63, *62*, *63*
properties of, *90*, 90–91, *91*
solvent mixtures and, 99–105, *100*, *101*, *102*, *103*, *104*
ammonium citrate, use on unvarnished paintings, 9

barrier paper, 186, 189, **190**, 191, *192*, 192, **194**
binary solvent mixtures
behavior of, 97–105, *100*
leaching resulting from, 100, 102–5, *102*, *103*, *104*
swelling responses to, 99–100, *100*, *101*
borax, 13, 201–2

carbonated distilled water, 144
cavitation energy, 98, *98*
chelating agents, 14, 21, 126, 140–44, 181
chromium oxide green, water sensitivity of, 109, 110, **110**, 111, *111*, *112*
cleaning
of acrylic paintings (*see* acrylic paints)
of alkyd paintings, 94 (*see also* alkyd paint)
definition of, 11, 45
dry (*see* dry cleaning)
laser, *206*, 209, 237–38
leaching resulting from (*see* leaching)
of modern paintings (*see* acrylic paints; polyvinyl acetate (PVAc) paints)
of oil paintings (*see* oil paint)
oxalate films and, 85–87
of plywood panel paintings, 175–77
simple, 13
of unvarnished paintings (*see* unvarnished paintings)
visual changes resulting from, 12
water-based (*see* water-based cleaning)
of water-stained areas, 205–7
commercial soap, 185–86. *See also* Vulpex
condition report, 10
conductivity, effect on water solubility of, 115–17, **117**
copaiba balsam, 8
cosolvation, 98
in alkyd paint systems, 99, 105

dammar, 77
binding medium effect on removal of, 81–82
canvas support and removal of, 82, **234**
color change on removal of, 80–81, *81*
effects of varnishing with, 78, *80*, 80
ground components and removal of, 82
size layer effect on removability of, 82
solubility of, 78
deionized water, oil paint sensitivity to, 109, 116, 117
dry cleaning
of oil paintings, 210, **213–14**, 214, *216*, *217*
of unvarnished paintings (*see* dry cleaning, unvarnished paintings)
dry cleaning, unvarnished paintings, 209–18
abrasion caused by, 214, *215*, *216*
products for, **210–11**
residues left from, 215–16, *217*, *218*, 229–31
Schlürfer vacuum use for, 221

egg tempera, 39
chemistry of, 39–40
effect of dry swabs on, 42, *42*, 43
effect of solvents on, 40–44
effect of water on, 40–43, *42*, *43*
emulsions, 126
effects on acrylic paints, *131*, 132–33, *132*, *133*
enzymes, hydrolytic, 181–82
cleaning with, *182*, 182–83
ethanol
effect on egg tempera, 40, 41, 42, *42*, 43
effect on polymeric films, **166**

foam cleaning, 225–27

gels, 21, 126, 179–80
effects on acrylic paints, *131*, 132–33, *132*, *133*
polyvinyl acetate (PVAc), 201–3
rigid (*see* rigid gels)
tissue, 197–99
Golden Polymer Varnish, 170, 172, **172**
gouache paint, 175
dry cleaning of, 210, *212*, **212**, **213–14**, *215*, *217*, *218*
grounds, color change in nineteenth-century, 77–84

heat, effect on oil paint, 56–57, *57*
hexane, effect on oil paint, 56, 57, **57**

ionic liquids, 233–35
ion migration, effects of, 64–65, *65*
isooctane
effect on egg tempera, *41*, 41–43, *42*, *43*
effect on polymeric films, **166**
Italy
current cleaning methods in, 20–21
late twentieth century cleaning methods in, 17–21
water-based cleaning in, 20–21

laser cleaning, *206*, 209, 237–38
leaching, 45, 69
of aged oil paint, 47, 48
of alkyd paint, 102–4, *102*, *103*
of new oil paint, 45–46
lead compounds
and alkyd paint durability, 62–63, *63*
and oil paint durability, 57, *57*, 60–61, *60*, *61*, 63–65, *64*, *65*
linseed oil paint, effect of solvents on, 52

margin test, 13
metal ions
and drying time of oil paint, 53, *54*, 54–55, 59–60
and oil paint stability, 55, *56*, 64–65, *65*
metal soaps, 43, 47, 122, *123*
Mineral Spirit Acrylic Gloss Varnish (MSA), 169–70, 171
Modular Cleaning Program (MCP), 140–41, 143–44, 145

National Gallery, London, cleaning controversy, 8, 9

oil paint
aging process of, 46–47
autoxidation of, 52–54, 59–60
chemistry of, 51–56
dry cleaning of, 210, **213–14**, 214, *216*, *217*
hydrolysis of, 54
pigments and (*see* pigments)
reducing drying time of, 53, *54*, 54–55
solvent effect on (*see* solvents)
solvent mixtures effect on, 99–100, *100*, *101*
stability of, 55–56, *56*
water sensitivity of, 107–14
oil paintings
cleaning of (*see* oil paint)
unvarnished (*see* unvarnished paintings)
water-sensitive, 107, 109, 115–17
See also oil paint
optical coherence tomography (OCT), 27–29
advantage of, 27
disadvantage of, 27
overpaint removal, OCT use in, 27–29, *28*
oxalate surface layers, 85–87
formation of, 86

paintings
aging of (*see* patina)
cleaning of (*see* cleaning)
nineteenth century cleaning of, 2–3, 8
oil (*see* oil paintings)
pre-nineteenth century cleaning of, 1–2
reasons for cleaning, 9, 239–40
twentieth century cleaning of, 3–4
unvarnished (*see* unvarnished paintings)
patina
nineteenth century view of, 2–3
pre-nineteenth century view of, 1–2
preservation of, 2
twentieth century view of, 3–4
paper
dry cleaning of, 14
wet cleaning of, 14
pH
effect on cleaning acrylic paintings, 141–42, 153
risks posed by high, 186
pigments
and durability of alkyd paint, 62–63, *63*
and durability of oil paint, 57, **57**, *60*, *61*, *62*, 60–62, 63–64, *64*
and water sensitivity of acrylic paint, *127*, 127, *128*, 128
and water sensitivity of oil paint, 108–14
and water sensitivity of polyvinyl acetate (PVAc) paint, *127*, 127, *128*, 128
plywood panels, paintings on, 175–77

polyvinyl acetate (PVAc) gels, 201–3
polyvinyl acetate (PVAc) paints
  additives, 132
  aging effects on, 136, *136*
  eraser effects on, 135–36, *137*
  solvent effects on, 129–30, *130*, 135–36, *137*
  water immersion effects on, 127–28, *128*, *129*, *130*, 136, *137*
  water sensitivity of, *127*, 127
pop art paintings, 175–77
poppy oil, 9, 13
  effect of solvents on paint based on, 52
PVAc gels. *See* polyvinyl acetate (PVAc) gels
PVAc paint. *See* polyvinyl acetate (PVAc) paints

raw sienna, water sensitivity of, 109, 110, **110**, 111, *112*
restoration
  art historian role in, 9
  condition report role in, 10, 31
  conservator role in, 9, 11, 12, 31–32, 240
  early science involvement in, 8, 9
  goals of, 9
  historical oversight of, 2
  nineteenth century view of, 2–3
  pre-nineteenth century view of, 1–2
  science role in, 9
  twentieth century view of, 3–4
rigid gels
  advantages of, 179, 180
  cleaning with, 180–81
  limitations on use of, 181
  use on plaster sculptures, 181

saliva, 13, 14
  artificial, 21, 182
  cleaning tests, 119–23, **122**
  oil paint sensitivity to, 109–10, **110**
Schlürfer, 221–22, *222*
sculptures, rigid gel use on plaster, 181
solubility triangle, 35. *See also* Teas solubility diagram
Soluvar Gloss Picture Varnish, 169–70, 171
solvation, 98
  of oil paint systems, 99
  selective, 98
solvent mixtures. *See* binary solvent mixtures
solvents
  damage caused by nineteenth century, 8
  effectiveness of, 35, *36*, *37*, 38, 126
  effects of use of, 8, 13–14, 82 (*see also specific solvent*)
  effects on acrylic paint, 129–30, *131*
  effects on aged oil paint, 47
  effects on egg tempera, 40–44, *41*, *42*, *43*
  effects on oil paint, 56, *57*, **57**
  effects on polymeric films, 165–67, **166**
  effects on polyvinyl acetate (PVAc) paint, 129–30, *130*
  leaching caused by (*see* leaching)
  mixtures of (*see* solvent mixtures)
  pigments and (*see* pigments)
  swelling power of (*see* swelling)
  traditional types of, 13
  See also specific solvent
Solvent Solver, 35, *37*
stratigraphic unit (SU), 31–33, *33*
surface abrasion, analysis of, *24*, 24–25
surfactants, 126
  and acrylic paints, 144–45, 149, 151, 153, *154–55*
  migration of, 160–61, *160*, *161*, 162
  removal of surface, *161*, 161–63, **162**
  wet cleaning and surface, **162**, 162–63
swabbing, alternatives to, 126, 197–99
swelling, 70
  of acrylic paints, 127, 130, 132, 133, 143, 149–50, *151–52*, 153
  of polyvinyl acetate (PVAc) paints, 130, 133
  power, 70, *72*, **72**, 72–76
  rate of, 72, **72**
  responses to individual solvents, 70–73, *70*, *71*, *72*, **72**, *73*, 74–75, *75*
  responses to mixtures of solvents, 74, *74*, 99–100, *100*, *101*

Teas solubility diagram, 13, 70, *73*
  limitations of, 73–74
textiles
  dry cleaning of, 14
  wet cleaning of, 14
time, effects of. *See* patina
titanium dioxide
  and durability of oil paint, 61, **61**
  and durability of alkyd paint, 63, *63*
toluene
  effect on oil paint, 56, *57*, **57**, 65
  effect on polymeric films, **166**
  swelling caused by, 70, *75*
toxicity, of cleaning substances, 19
Triansol, 35, 38
Trisolv, 35, *37*

ultramarine blue
  varnish removal and, 171, 172, *173*
  water sensitivity of, 109–11, **110**, *111*, *113*, 113
unvarnished paintings, 77, 84
  cleaning of, 9, 14, 107–14, 115–17, 119–23, 175–77, 209–18
  commercial soap use on, 185–94
  dry cleaning of (*see* dry cleaning, unvarnished paintings)
  used as benchmarks for varnish removal, 83
  varnishing of, 9, 77
urine, 13

varnish
  degradation of, 12, 13
  effects of, 12, 77, 78, *80*, 80
  Impressionist paintings and, 13, 77, 82
  modern period use of, 13
  purpose of, 12
  removal of (*see* varnish removal)
  solvents and removal of (*see* solvents)
  undried paint and, 12–13
  washing (*see* water-based cleaning)
varnish removal
  abrasion method of, 13
  from acrylic paints, 169–73
  binding medium and, 81–82
  canvas support and, 82
  color change upon, 80–81, *81*
  ground components and, 82
  historical methods of, 8, 9, 12, 13
  ionic liquids use in, 233–35, *234*
  issues in, 82–84
  lining and, 82
  Schlürfer vacuum use in, 222, *223*
  size layer and, 82
  solvent use in (*see* solvents)
  tissue gel technique for, 197–99
  water-based systems for, 14
  See also varnish

water-based cleaning, 13, 14, 20–21, 179–80
  of acrylic paintings, 48
  effect on egg tempera, 40–43, 42, *42*, *43*
  foam, 225–27
  See also oil paint: water sensitivity of

Vulpex, use on unvarnished paintings, 186–94
  residues left by, *188*, 188–90, *189*, **190**
  surface damage caused by, 190–94, *191*, *192*, *193*, **194**, *195*

xylene
  effect on polymeric films, **166**
  swelling caused by, 70, *75*

zinc oxide
  and durability of alkyd paint, 62, *63*
  and durability of oil paint, *57*, **57**, 61, *61*, 64–65

REQUIREMENTS FOR SMITHSONIAN SERIES PUBLICATION

ALL MANUSCRIPTS ARE REVIEWED FOR ADHERENCE TO THE SISP MANUSCRIPT PREPARATION AND STYLE GUIDE FOR AUTHORS (available on the "Submissions" page at www.scholarlypress.si.edu). Manuscripts not in compliance will be returned to the author. Manuscripts intended for publication in the Contributions Series are evaluated by a content review board and undergo substantive peer review. Accepted manuscripts are submitted for funding approval and scheduling to the Publications Oversight Board.

MINIMUM MANUSCRIPT LENGTH is thirty manuscript pages. If a manuscript is longer than average, an appropriate length will be determined during peer review and evaluation by the Content Review Board. Authors may be asked to edit manuscripts that are determined to be too long.

TEXT must be prepared in a recent version of Microsoft Word; use a Times font in 12 point for regular text; be double spaced; and have 1" margins. Each chapter/section must be saved in a separate file.

REQUIRED ELEMENTS are title page, abstract page, table of contents, main text, and reference section. See the SISP Manuscript Preparation and Style Guide for Authors for the order of all elements.

HEADINGS should be styled so different levels of headings are distinct from each other and so the organization of the manuscript is clear. Insert one line space above and one line space below all headings.

FRONT MATTER should include title page, abstract page, and table of contents. All other sections are optional. Abstracts must not exceed 300 words. Table of contents should include A-, B-, and C-level headings.

TABLES (numbered, with captions, stubs, rules) should be submitted in separate MS Word files; should include footnotes, if appropriate; should have rules only at top, bottom, and beneath column heads. Print outs of each table should accompany the manuscript to ensure correct layout of data. Tabulations within running text should not be numbered or formatted like formal tables, and should be included in the text of the manuscript.

FIGURE CAPTIONS should be provided in a separate MS Word file.

FIGURES (e.g., photographs, line art, maps) should be numbered sequentially (1, 2, 3, etc.) in the order called out; be placed throughout text, not at end of manuscript; have all components of composites lettered with lowercase letters and described in the caption; include a scale bar or scale description, if appropriate; include any legends in or on the figure rather than in a caption.

ART must not be embedded in the main text.

Figures must be original and submitted as individual TIFF or EPS files. Resolution for art files must be at least 300 dpi for grayscale and color images and at least 1200 dpi for line art. Electronic images should measure no more than 100% and no less than 75% of final size when published. JPG files will not be accepted. Color images significantly increase costs so should be included only if required. Funding for color art is subject to approval by SISP and the Publications Oversight Board.

TAXONOMIC KEYS in natural history papers should use the aligned-couplet form for zoology. If cross referencing is required between key and text, do not include page references within the key but number the keyed-out taxa, using the same numbers with their corresponding heads in the text.

SYNONOMY IN ZOOLOGY must use the short form (taxon, author, year:page), with full reference at the end of the paper under "References."

IN-TEXT REFERENCES should be used rather than bibliographic notes and should follow the author-date system in the following format: "(author last name, year)" or ". . . author (year)"; "(author, year:page used within the text)" or ". . . author (year:page)." A full citation should be included in a "References" section.

ENDNOTES are to be used in lieu of footnotes and should be keyed manually into a separate MS Word file, in a section titled "Notes". Notes should not contain bibliographic information. Manually type superscript numerals in text and use full-sized numerals at the beginning of each note in the "Notes" section. SISP will determine the best placement of the notes section, either at the end of each chapter or at the end of the main text.

REFERENCES should be in alphabetical order, and in chronological order for same-author entries. Each reference should be cited at least once in main text. Complete bibliographic information must be included in all citations (e.g., author/editor, title, subtitle, edition, volume, issue, pages, figures). For books, place of publication and publisher are required. For journals, use the parentheses system for volume(number):pagination [e.g., "10(2):5–9"]. Do not use "et al."; all authors/editors should be included in reference citations. In titles, capitalize first word, last word, first word after colon, and all other words except articles, conjunctions, and prepositions. Examples of the most common types of citations are provided in the SISP Manuscript Preparation and Author Style Guide.

For questions regarding the guidelines, please email SISP at schol.press@si.edu.