

Deterioration in Abstract Expressionist Paintings: Analysis of Zinc Oxide Paint Layers in Works from the Collection of the Hirshhorn Museum and Sculpture Garden, Smithsonian Institution

Christopher A. Maines¹, Dawn Rogala², Susan Lake³, and Marion Mecklenburg²

¹National Gallery of Art, Washington DC 20565, U.S.A.

²Museum Conservation Institute, Smithsonian Institution, Landover MD 20785, U.S.A.

³Hirshhorn Museum and Sculpture Garden, Smithsonian Institution, Washington DC 20560, U.S.A.

ABSTRACT

A recent visual survey of Abstract Expressionist-era paintings in the collection of the Hirshhorn Museum and Sculpture Garden (HMSG), Smithsonian Institution revealed a particular type of paint layer separation. Earlier work by the authors showed that zinc oxide in oil paint is a contributing factor to the problem. Ten samples from five Abstract Expressionist-era paintings as well as twenty-three samples eight years or older from the Smithsonian Institution's (SI) Materials Study Collection were analyzed by pyrolysis – gas chromatography – mass spectrometry (Py-GC-MS), and unexpectedly significant amounts of oleic (*cis*-octadecenoic) acid were detected in samples containing high proportions of zinc oxide (25 % or greater by weight). In a typical fully cured oil paint, the oleic acid is oxidized to azelaic (nonanedioic) acid. Although the formation of zinc soaps in oil paints is well-known, the detection of zinc oleate in paints by Py-GC-MS has never been described. The close-packing of the oleate chains in the plate-like structure of zinc oleate prevents the oxidation of the *cis*-double bond, and therefore prevents the formation of azelaic acid. The detection of zinc oleate in paintings is an indication that the paint layers are at risk for future separation.

INTRODUCTION

In 2007, a visual survey of the approximately 4,600 paintings in collection of the Hirshhorn Museum and Sculpture Garden (HMSG), Smithsonian Institution revealed a particular type of paint layer separation in certain mid-twentieth century paintings (figure 1). Closer visual and instrumental inspection revealed the cleaving paints to be applied over paints containing significant amounts of zinc oxide, which was shown to be a contributing factor to the problem [1].

The phenomenon of lead, zinc and copper fatty acid metal soaps is well documented in conservation literature with much attention having been paid to lead soaps in old master paintings [2-5]. The brittle nature of zinc oxide paints used in industrial and artists' paints, as well as artists' use of industrial paints, have been well-documented in the early twentieth-century literature [6-10]. Recent conservation literature has also highlighted the brittle nature of zinc oxide paints [11-12]. Work by Jacobsen and Gardner in 1941 showed that zinc forms crystals with fatty acids in linseed oil paint films, and they proposed a crystalline structure of alternating layers of zinc and oleate based on x-ray powder diffraction and stoichiometry [13]. Barman and Vasudevan recently confirmed the close packing of oleate (*cis*-octadecenoate) chains in layers alternating with zinc by x-ray powder diffraction (XRD), differential scanning calorimetry (DSC) and Fourier-transform infrared spectroscopy (FT-IR) [14]. This paper will show that

pyrolysis – gas chromatography – mass spectrometry (Py-GC-MS), a technique proven to be useful in the analysis of natural and synthetic binding media in twentieth-century paintings, can also be used to reveal the presence of zinc soaps in oil paint layers through the detection of oleic acid.



Figure 1. Detail of intralayer cleavage in *Magic Doll with Pig's Head*, 1961 (HMSG 66.65) by Karel Appel. The larger arrows mark the intralayer cleavage in the zinc oxide-rich cadmium red paint layer. The smaller arrows mark the intralayer cleavage in the zinc white ground layer. This double intralayer cleavage within two adjacent layers of zinc oxide-rich paints leads to a very thin layer of cleaving paint – one side being cadmium red paint and the other being zinc white ground – demonstrating that there is no interlayer adhesive failure.

EXPERIMENT

Paint Samples

Eighteen Abstract Expressionist-era paintings from the HMSG collection were examined by, variously, XRF, SEM-EDS, optical microscopy, and FT-IR as described previously [1]. Samples from works by Karel Appel (HMSG 66.65 – two samples), Hans Hofmann (HMSG 66.2483 – two samples, and HMSG 66.2477 – two samples), and Franz Kline (HMSG 66.2754 – two samples) were analyzed by pyrolysis – gas chromatography – mass spectrometry (Py-GC-MS). The sample of the zinc oxide-containing ground layer from the Kline painting was

described previously in the earlier research [1]. All ten samples were found to contain drying oil binders. No alkyds or synthetic polymeric binding media were detected in any of the samples.

In addition, twenty three samples from various paint films in the Smithsonian Institution's (SI) Materials Study Collection housed at the Museum Conservation Institute (MCI) were analyzed by Py-GC-MS. These samples were all of known composition: they were either controls made at the request of SI by Gamblin Artists Colors from known starting materials, or the manufacturers of the commercially available paints confidentially disclosed the components and proportions used. In brief, the manufacturers' commercial paints consist primarily of drying oils and pigments and contain only small percentages of additional saturated fatty acid soaps with no additional oleates. The paints made at the request of SI by Gamblin Artists Colors contain only the pure drying oils and pigments. The paint films were cast at various times between March 1978 and September 2000, and were therefore at least eight years old at the time of the Py-GC-MS analyses [15-16].

X-ray Fluorescence

Paintings were examined using a Bruker Tracer III-V handheld energy dispersive X-ray Fluorescence spectrometer (ED-XRF). The instrument has a miniature X-ray tube with a Rhodium anode, a Si PIN diode detector, and was operated at 35 keV and 15 μ Amps, using a Cu-Al-Ti filter without vacuum. The instrument beam spot size is approximately 3 mm in diameter. Resolution is 149 eV FWHM at 5.9 keV. For these analyses, the portable XRF unit was used in a stationary mode on a tripod. In this configuration, good contact with the object is optimized as much as possible with the instrument window. Exposures are set for 120 seconds in order to maximize the signal to noise ratio.

Scanning Electron Microscopy-Energy Dispersive Spectroscopy

Samples were imaged and analyzed using a Hitachi S3700-N scanning electron microscope and a Bruker XFlash energy dispersive spectrometer with Quantax 400 software. The samples were received after they had been prepared for and imaged by polarized light microscopy. They were carbon coated before analysis. The SEM was operated at 20 to 25 kV, at full vacuum. Elemental maps were generated over 300 seconds real time (with 0–18% dead time). Spot and area analyses were conducted for 200 seconds live time. Analyses were conducted at a working distance between 9.8 and 10.2 mm.

Pyrolysis-Gas Chromatography-Mass Spectrometry

Samples were analyzed using a Varian Saturn 2000 GC/MS equipped with a CDS Pyroprobe 2000. Each sample was placed into a quartz boat along with two microliters of tetramethylammonium hydroxide (TMAH) as a methylating reagent for the fatty acids. The boat was placed into the coiled platinum probe of a CDS Pyroprobe 2000 filament pyrolysis unit, placed into a CDS 1500 Valved Interface at 310°C and purged with helium for 10 seconds before opening the valve to the GC column. The sample was then heated with the pyroprobe to a temperature of approx. 600°C for 10 seconds. The pyrolysis products were transferred directly to a capillary column (ZB-5ms; 30 m x 0.25 mm i.d.; 0.25 micron film thickness; He flow of 1.2 ml/min; splitless.) in a Varian 3800 gas chromatograph (GC) and then to a Varian Saturn 2000

ion trap. The GC oven was programmed with an initial temperature of 30°C, which was held for 5 minutes. The temperature was increased at a rate of 10°C per minute to 300°C and held for 10 minutes. The Varian Saturn 2000 ion trap conditions were as follows: transfer line at 270°C, trap at 150°C, manifold at 80°C; electron multiplier at 1500 V; scan range 45-650 amu; scan time 1 second.

DISCUSSION

The purpose of the earlier study by Rogala et al. was to discover why areas within certain Abstract Expressionist-era paintings were showing similar signs of failure in paint layer adhesion [1]. Through analysis by XRF, SEM-EDS, and optical microscopy of the paint layers taken from these areas, it was shown that the brittle nature of the zinc oxide-containing paints led to mechanical failure, and that cleavages in the paint were occurring within the paint layers themselves and were not failures of adhesion between different layers of paint. Figure 1 shows a detail from *Magic Doll with Pig's Head*, 1961 (HMSG 66.65) by Karel Appel illustrating two such intralayer cleavages occurring in adjacent layers of paint that each contain well over 60% zinc oxide (mean wt. % oxide content).

The earlier study also showed that significant amounts of zinc oxide in a drying oil could be inferred from Py-GC-MS analysis of the binding medium. In Rogala et al., Py-GC-MS analyses of two samples from *Palladio* (HMSG 66.2754) by Franz Kline and two samples from the SI Materials Study Collection – each set of samples containing paints with and without zinc oxide – showed that the paints containing significant amounts of zinc oxide also contained significant amounts of methyl oleate compared to methyl stearate (octadecanoate) (peak area ratio of oleate:stearate of app. 1:3), while the paints containing no zinc oxide showed no evidence of methyl oleate [1].

It is well known that during the typical curing process of a drying oil, such as linseed or safflower oil, the unsaturated fatty acid side-chains on the glycerol backbone either become part of the cross-linked polymeric network through autoxidation or become free fatty acids through hydrolysis. Free oleic acid is typically completely converted by oxidation to azelaic acid in a fully cured paint film. In the gas chromatographic analysis of a drying oil using a methylating derivatization reagent either during sample preparation or *in situ*, the three resulting primary components of the analyte are dimethyl azelate, methyl palmitate (hexadecanoate), and methyl stearate. The presence of more than a trace amount of methyl oleate is interpreted as an indication that the paint film is either not yet fully cured or that something has interfered with the curing process. The ratio of the peak areas of methyl palmitate to methyl stearate is often considered to be indicative of the type of drying oil present [17], although the frequent addition of metal salts of fatty acids to twentieth-century paint formulations – primarily metal stearate salts – suggests caution when interpreting these ratios in the analysis of paintings from this era.

Comparison of the previously published Py-GC-MS results with the Py-GC-MS results from the other eight samples described above, as well as the additional twenty one samples from the SI Materials Study Collection reveal the same phenomenon: paints containing significant amounts of zinc oxide (25% by weight or more) show significant amounts of methyl oleate (peak area ratio of oleate:stearate of app. 1:1). Conversely, Py-GC-MS analyses of paints without zinc oxide show no appreciable amounts of methyl oleate.

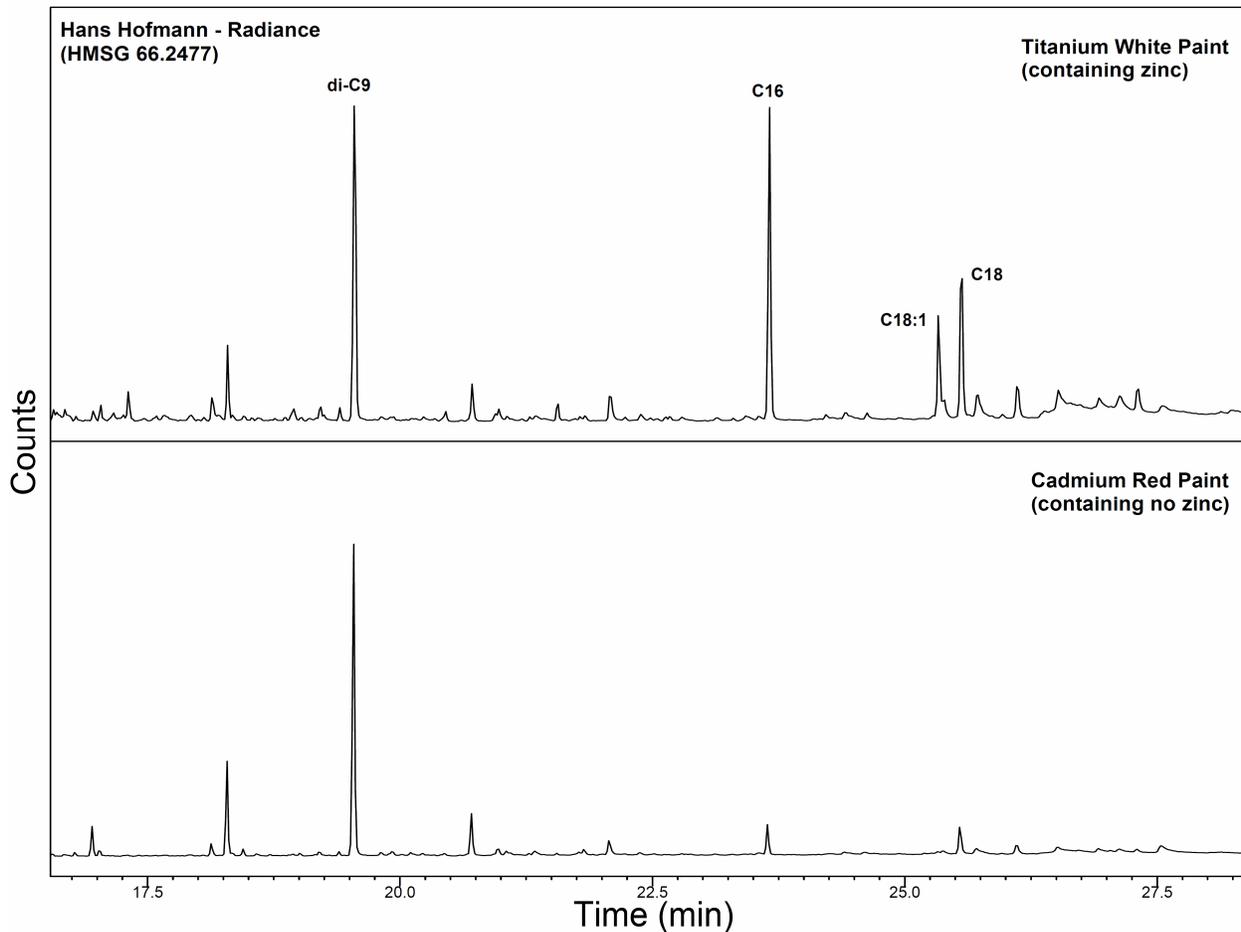


Figure 2. Chromatograms from Py-GC-MS analyses of the binding media of the upper and lower layers of paint from *Radiance* (HMSG 66.2477) by Hans Hofmann. di-C9 = dimethyl azelate, C16 = methyl palmitate, C18:1 = methyl oleate, C18 = methyl stearate. Both chromatograms identify the binding media as drying oils. No alkyds or synthetic polymeric binding media are present.

The upper chromatogram is that of a ground layer of titanium white paint that contains app. 40% zinc oxide (mean wt. % oxide content) as shown by SEM-EDS. The lower chromatogram shows a cadmium red paint from an upper visible layer that contains no zinc. The upper chromatogram shows a significant amount of methyl oleate – well more than 50% of the amount of methyl stearate, while the lower chromatogram shows a negligible amount of methyl oleate. The presence of methyl oleate is from the formation of a close-packed layered structure of zinc and oleate that inhibits oxidation of oleic acid to azelaic acid. Intralayer cleavage in the zinc white ground is allowing the cadmium red paint to lift away at many locations throughout the painting.

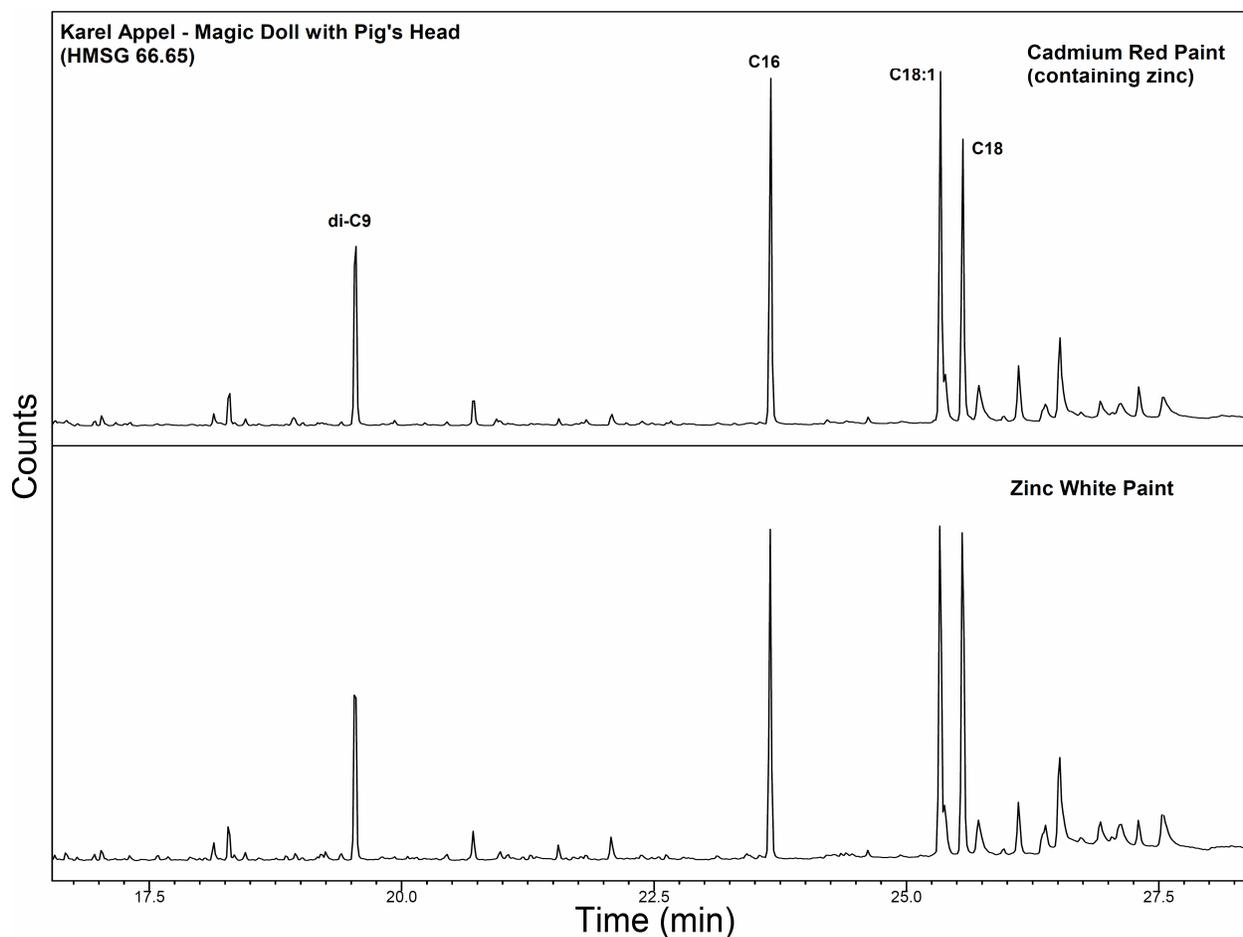


Figure 3. Chromatograms from Py-GC-MS analyses of the binding media of the upper and lower layers of paint from *Magic Doll with Pig's Head* (HMSG 66.65) by Karel Appel. di-C9 = dimethyl azelate, C16 = methyl palmitate, C18:1 = methyl oleate, C18 = methyl stearate. Both chromatograms identify the binding media as drying oils. No alkyds or synthetic polymeric media are present.

The upper chromatogram is an upper layer of cadmium red paint that contains app. 50% zinc oxide (mean wt. % oxide content) as shown by SEM-EDS. The lower chromatogram is from a ground layer of zinc white paint. Both samples show unexpectedly significant amounts of methyl oleate – the peak area ratio of methyl oleate to methyl stearate is roughly 1:1. The presence of methyl oleate is from the formation of a close-packed layered structure of zinc and oleate that inhibits oxidation of oleic acid to azelaic acid. Intralayer cleavage in the zinc white ground is allowing the cadmium red paint to lift away at many locations throughout the painting.

Figure 2 shows the chromatograms from the Py-GC-MS analyses of two paint samples from *Radiance*, 1956 (HMSG 66.2477) by Hans Hofmann – a zinc-titanium mix white underlayer and the cadmium red paint directly above that layer. The zinc-titanium mix shows a significant amount of methyl oleate (peak area ratio of oleate:stearate of app. 3:4) while the cadmium red paint, which contains no zinc, shows no methyl oleate. Figure 3 shows the chromatograms from the Py-GC-MS analyses of two paint samples from *Magic Doll with Pig's Head*, 1961 (HMSG 66.65) by Karel Appel – a zinc-containing cadmium red paint and a zinc

white ground layer. Both chromatograms show significant amounts of methyl oleate (peak area ratio of oleate:stearate of 1:1). SEM-EDS analyses of the four paint samples show that those containing significant amounts of methyl oleate have zinc oxide contents between 37% and 75% (mean wt. % oxide content), while the cadmium red paint showing no methyl oleate has no zinc oxide.

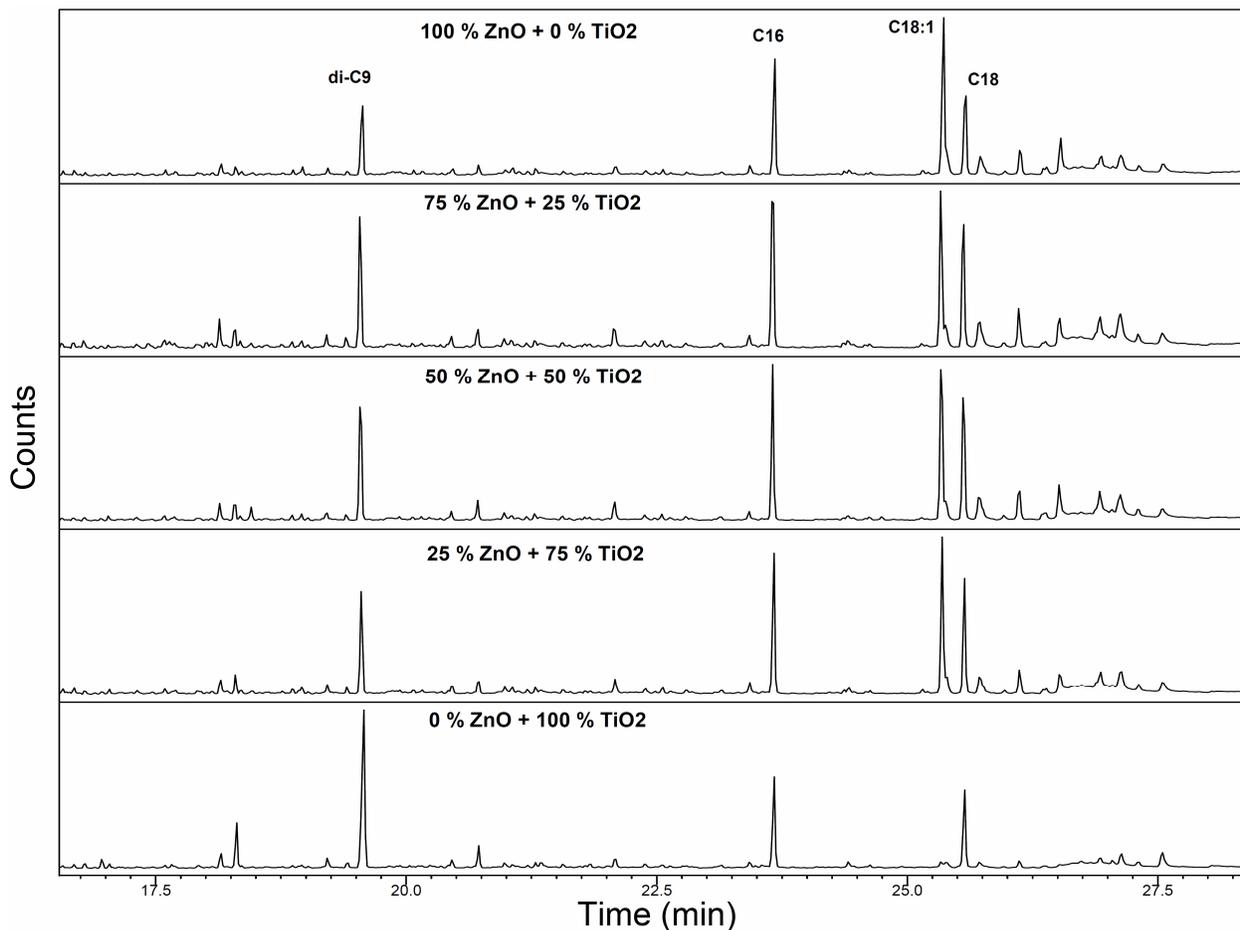


Figure 4. Chromatograms from Py-GC-MS analyses of binding media of paints consisting only of various proportions of titanium dioxide and zinc oxide pigments in alkali-refined linseed oil prepared and cast specially by Gamblin Artists Colors for M. Mecklenburg in September, 2000. di-C9 = dimethyl azelate, C16 = methyl palmitate, C18:1 = methyl oleate, C18 = methyl stearate. The paint containing 100% titanium dioxide (wt. % pigment) shows no methyl oleate as expected in a fully cured drying oil film. The paints containing 25% to 100% zinc oxide show the presence of methyl oleate, which is not expected in a fully cured drying oil film. The presence of oleic acid is from the formation of a close-packed layered structure of zinc and oleic acid that inhibits oxidation of oleic acid to azelaic acid. As the amount of methyl oleate present is relatively invariant between 25% and 100% zinc oxide, the amount of free oleic acid available for forming zinc soaps must be completely involved by at least 25% if not somewhat below.

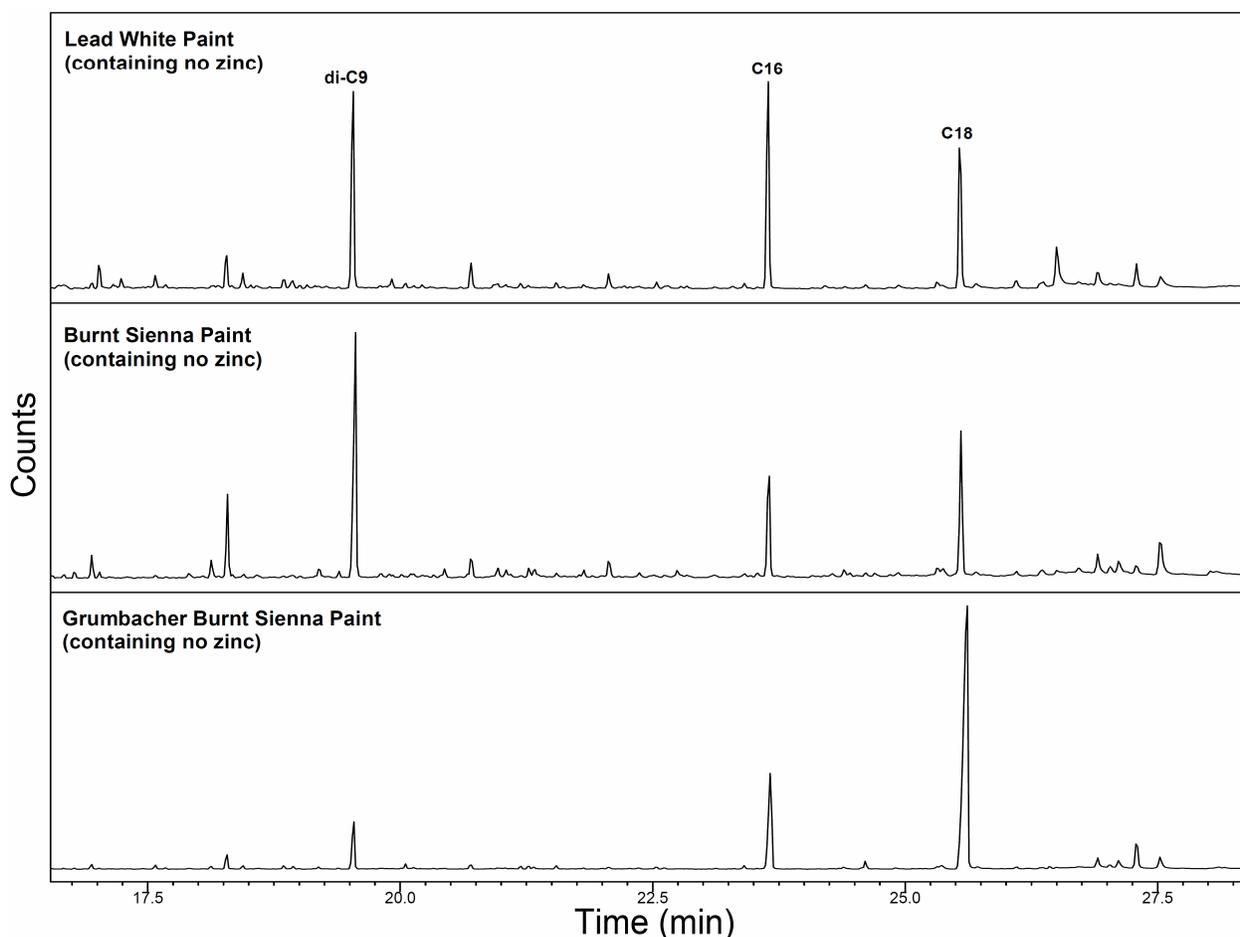


Figure 5. Chromatograms from Py-GC-MS analyses of binding media of paints from the SI Materials Study Collection. di-C9 = dimethyl azelate, C16 = methyl palmitate, C18:1 = methyl oleate, C18 = methyl stearate.

The lead white paint was made by Gamblin Artists Color for M. Mecklenburg from lead white pigment in cold-pressed safflower oil and cast in March, 1990. The burnt sienna paint was made by Gamblin Artists Color for M. Mecklenburg from burnt sienna pigment in cold-pressed linseed oil and cast in January, 1999. The Grumbacher burnt sienna paint was made from burnt sienna pigment in alkali-refined linseed oil and cast at the SI in November, 1978. As expected, although the drying oils and their preparations are different, none of the three chromatograms show significant amounts of methyl oleate. The large methyl stearate peak in the chromatogram of the Grumbacher burnt sienna is a result of additional metal stearates in Grumbacher's drying-oil paint formulation, and is a good example of why it is not advisable to rely on methyl palmitate to methyl stearate ratios to determine the identity of a drying oil in a twentieth-century paint.

The results are similar for the samples from the SI Materials Study Collection (figures 4 and 5). Five samples of varying proportions of titanium white and zinc white in alkali-refined linseed oil show definitively that significant amounts of methyl oleate will be seen in Py-GC-MS analyses when at least 25% zinc oxide (wt. % pigment) is present (figure 4). As the amount of methyl oleate present is relatively invariant between 25% and 100% zinc oxide, the amount of free oleic acid that is available for forming zinc soaps is inferred to be completely involved by at

least 25%, or possibly lower. The chromatograms from the Py-GC-MS analyses of three SI Materials Study Collection samples that contain no zinc oxide (figure 5) show that without zinc oxide, no significant amount of methyl oleate is observed in fully cured films of drying oils. It is well-known that lead forms soaps with free fatty acids in drying oils, but no one has previously reported the significant amounts of methyl oleate consistent with the results in this study.

Since oleic acid is detected in significant amounts in fully cured films of zinc oxide-containing oil paint, oxidation of the *cis*-double bond is being prevented. The most reasonable explanation for this phenomenon is that the oleic acid chains are in a crystalline state which prevents oxidation from occurring. Work by Jacobsen and Gardner in 1941 showed that zinc forms crystals with fatty acids in linseed oil paint films. From the stoichiometry of the reaction of oleic acid with zinc oxide and x-ray powder diffraction data of the crystals formed, Jacobsen and Gardner proposed the structure of zinc oleate crystals to consist of alternating layers of zinc complexed with oleate ions: each zinc ion is coordinated with four oleate ions by carboxylate bridges – two above and two below “sandwiching” the zinc – such that the oleate ions from adjacent layers separate the layers of zinc ions [13]. As noted above, work by Barman and Vasudevan in 2006 confirms this structure and also demonstrates that zinc oleate and zinc stearate together can form solid solutions, unlike oleic and stearic acids, which will only crystallize separately [14].

In this respect, the formation of zinc soaps in oil paint is quite different from the well-documented formation of lead soaps in oil paintings [2-5]. The formation of lead oleate has not been observed in oil paintings, although lead azelate has been observed [18]. Lead soaps form macroscopically observable “pustules” or “protrusions,” while zinc soaps exhibit plate-like formations. The kinetics of these soap formation reactions in oil paints is unclear, and therefore it can only be surmised that the formation of zinc oleate is rapid enough to prevent the oxidation of oleic acid to azelaic acid, while the formation of lead oleate does not occur because it is either too slow or not favorable. It could also be suggested that the layered structure of zinc soaps and their rapid formation may contribute to weaker adhesion within the paint film, thus leading to the intralayer cleavage that seems to be prevalent in these Abstract Expressionist-era zinc oxide-containing oil paints.

CONCLUSIONS

Zinc oxide-containing oil paints in Abstract Expressionist-era paintings have been detected through Py-GC-MS analyses of the binding media by the presence of significant amounts of oleic acid (peak area ratio of oleate:stearate of at least 1:3). The presence of a significant amount of oleic acid in a fully cured oil paint indicates not only that zinc oleate has formed from the presence of zinc oxide, but also that sufficient zinc oxide is present in the oil film to promote mechanical failure and intralayer cleavage. If XRF analysis indicates the presence of zinc in a paint film, Py-GC-MS can be a useful tool in determining whether a painting might be susceptible to intralayer cleavage.

ACKNOWLEDGMENTS

The authors wish to express their gratitude for the support of many people and institutions., including Stuart Croll, Professor and Chair, Department of Coatings and Polymeric Materials, North Dakota State University; Roland (Ron) H. Cunningham, Senior Paintings Conservator,

MCI; Melvin Wachowiak, Senior Conservator, MCI; and Judy Watson, former Physical Scientist, MCI. Funding for Rogala was provided by The Samuel H. Kress Foundation and The Smithsonian Institution Fellowship Program.

REFERENCES

1. D. Rogala, S. Lake, C. Maines, and M. Mecklenburg, *Journal of the American Institute for Conservation* **49** (3), in press (2010).
2. J. van der Weerd, PhD Thesis, AMOLF/University of Amsterdam, 2002.
3. J. van der Weerd, J. J. Boon, M. Geldof, R. M. A. Heeren, and P. Noble, *Zeitschrift für Kunsttechnologie und Konservierung* **16**, 36–51 (2002).
4. L. Robinet and M.-C. Corbeil, *Studies in Conservation* **48** (1), 23-40 (2003).
5. Y. Shimadzu, K. Keune, K. J. van den Berg, J. H. Townsend, and J. J. Boon, in *15th Triennial Meeting of the ICOM Committee for Conservation* (Allied Publishers Pvt Ltd, New Delhi, 2008), pp. 626-632.
6. R. Goodnough, *ARTnews* **51** (8), 36-39 (1952).
7. E. de Kooning, *ARTnews* **48** (10), 58-59 (1950).
8. G. Petit and D. Grant, *The manufacture and comparative merits of white lead and zinc white paints* (Scott, Greenwood and Son, London, 1907), p. 84.
9. R. W. Bailey and A. Pass, *Journal of the Oil and Colour Chemists' Association* **36** (April), 171-194 (1953).
10. F. C. Schmutz, *Official Digest - Federation of Paint and Varnish Production Clubs* **141**, 355-357 (1935).
11. M. F. Mecklenburg and C. S. Tumosa, in *Art in transit: studies in the transport of paintings* (National Gallery of Art, Washington DC, 1991), pp. 137-171.
12. M. F. Mecklenburg, J. D. Erlebacher, E. Brown, and C. S. Tumosa, in *Materials Issues in Art and Archaeology VI*, edited by P. B. Vandiver, M. Goodway, and J. L. Mass, (Materials Research Society **712**, Boston, MA, 2002) pp. 359-370.
13. A. E. Jacobsen and W. H. Gardner, *Industrial and Engineering Chemistry* **33** (10), 1254-1256 (1941).
14. S. Barman and S. Vasudevan, *Journal of Physical Chemistry B* **111**, 5212-5217 (2007).
15. M. F. Mecklenburg, C. S. Tumosa, and D. Erhardt in *Materials Issues in Art and Archaeology VII*, edited by P. B. Vandiver, J. L. Mass, and A. Murray, (Materials Research Society **852**, Boston, MA, 2005) pp. 13-31.
16. Y. Maor and A. Murray in *Materials Issues in Art and Archaeology VIII*, edited by P. B. Vandiver, B. McCarthy, R. H. Tykot, J. L. Ruvalcaba-Sil, and F. Casadio, (Materials Research Society **1047**, Boston, MA, 2007) pp. 127-136.
17. J. S. Mills and R. White, *The Organic Chemistry of Museum Objects*, 2nd ed. (Butterworth-Heinemann Ltd., Oxford, 1994), p. 33 and 171.
18. M. J. Plater, B. De Silva, T. Gelbrich, M. B. Hursthouse, C. L. Higgitt, and D. R. Saunders, *Polyhedron* **22**, 3171–3179 (2003).