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Electronic version
URL: https://journals.openedition.org/techne/16944
DOI: 10.4000/techne.16944
ISSN: 2534-5168

Publisher
C2RMF

Printed version
Date of publication: November 16, 2023
Number of pages: 14-25
ISBN: 978-2-11-167438-7
ISSN: 1254-7867

Electronic reference
Shawn Digney-Peer, Silvia A. Centeno, Julie Arslanoglu and Federico Carò, "Back in Black: getting beneath the haze on Adolph Gottlieb’s *Thrust*", *Technè* [Online], 55 | 2023, Online since 16 November 2023, connection on 25 November 2023. URL: http://journals.openedition.org/techne/16944 ; DOI: https://doi.org/10.4000/techne.16944

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Back in Black: getting beneath the haze on Adolph Gottlieb’s Thrust

Abstract. Thrust (1959) is an iconic example of Adolph Gottlieb’s series of “Bursts” (1956-1974). The painting is grand in scale and consists of an aggressive thrash of black, gestural strokes beneath a crimson, haloed disc, on a white background. Gottlieb said that given the limited palette, his color choices were critical in conveying the emotional quality of his work. The appearance of Thrust was compromised when efflorescence became visible on the surface in 1981; the material presented as a subtle white haze that made the black appear gray. By 1996, the effect had become more pronounced, and the painting was taken off view. Recent curatorial interest in displaying the painting motivated an evaluation of its condition and of treatment options. This paper discusses the painting’s materials and techniques, the composition of the efflorescence as investigated by spectroscopic and chromatographic methods, and considerations given to its treatment.

Keywords. Gottlieb (Adolph), abstract expressionism, efflorescence, fatty acids, metal soaps, matte paint, hot air pencil, heat treatment.


Mots-clés. Gottlieb (Adolph), expressionnisme abstrait, efflorescence, acides gras, savons métalliques, peinture mate, crayon à air chaud, traitement thermique.

“I want to express the utmost intensity of the color.”
Adolph Gottlieb

Adolph Gottlieb and Thrust

Adolph Gottlieb is one of the most prominent American artists of the mid-20th century. He is an early, and principal, protagonist in the story that would become known as abstract expressionism, and his work directly influenced the rise of color field painting. Gottlieb is most widely recognized for a series of paintings that he began in 1956. Collectively referred to as “Bursts”, they consumed his attention for seventeen years, until his death in 1974.

Each “Burst” is a subjective image whose meaning is intended to be deeply personal and identified by the subconscious of the viewer. The language Gottlieb used to achieve this was limited to three elements: a monochromatic background onto which is painted a “disc”, that is often suspended above a “blast”. The disc, spherical or elliptical in shape, is usually surrounded by a subtle halo that makes it appear to glow. The blast resembles an expanding tangled mass of gestural and more sharply defined forms.

Gottlieb stated: “...since I eliminated almost everything from my painting except a few colors and perhaps two or three shapes, I feel a necessity for making the particular colors that I use, or the particular shapes, carry the burden of everything that I want to express, and all has to be concentrated within these few elements. Therefore, the color has to carry the burden of this effort.”

*Thrust* (1959) is among the largest of all the “Bursts” and was created while Gottlieb was still defining the imagery (fig. 1). It is also a classic example of these paintings and is executed in the colors Gottlieb found most exciting for having “within themselves a certain charge”: white, red, and black.

### Materials and technique

Gottlieb began *Thrust* by stapling cotton duck canvas onto a foldable strainer of his own fabrication. He then re-stretched the canvas, likely after decrimping it. For the background, he laid down a thin, white, variably matte layer consisting of multidirectional strokes made with a brush and lengthwise strokes made with a roller. Several lengthwise streaks of paint were applied that fill the canvas weave more than the surrounding areas and appear glossy in specular light; it is not clear how these were achieved. As we discuss below, in cross-section these paint applications are indistinguishable from one another, suggesting a wet-in-wet technique.

With the painting face up on sawhorses (fig. 2 a), Gottlieb then created the black blast and the red disc. For the blast, he describes his process: “I get my paint in a rather viscous state so that it’s fluid, but not buttery, the way it comes out of the tube, and then I pour some of the paint on the canvas and it makes a puddle which is more or less a round puddle. It just takes that form by itself. And then I start manipulating this paint with a large spatula or a stick or a squeegee or whatever I feel will do what I want it to do, and I start flinging the paint out of this circular puddle in the direction I want it to go; and it’s as if the paint were then spun with a centrifugal motion and it flies in tangents, and it has to have the right viscosity so that it will handle and it will have the proper fluidity for this type of handling... And then, of course, if I decide it hasn’t spun out quite the way I want it to, I might drip it on a bit; but it isn’t primarily a dripping technique, which is done very differently...”

For the disc and halo, he describes: “I might put a disc, let us say, of red, and I’ll put it on with a spatula, just a big, flat disc. This is rather thick paint, even impasto. Then I might take a rag, soak it with turpentine, work around the edge, and develop something that is like a halo, so that I get this impasto-like color opposed to the very transparent, stained sort of color.”

For the black blast of *Thrust*, Gottlieb used a squeegee, likely followed by a brush. For the red disc, he used a palette knife. For the halo, he used a rag soaked in turpentine. The resulting surfaces have a variable gloss related to his materials and his techniques; overall, the blast is matte, the disc is glossy, and the halo is matte (fig. 2 b).

### Analysis of the materials

As mentioned above, Gottlieb began by applying a white layer onto the canvas, likely in more than one application, suggested by the image taken under UV illumination (fig. 3) that shows distinct areas that fluoresce green and purple. These applications were most likely done wet-in-wet...
as it is not possible to distinguish more than one layer by optical microscopy or scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) in the sample cross-section examined (fig. 4 a-c). Raman spectroscopy analysis of the white paint in this sample showed features characteristic of rutile at ca. 447 and 609 cm\(^{-1}\) and of barium sulfate at ca. 988 cm\(^{-1}\). The presence of barium sulfate and rutile particles was confirmed by micro X-ray diffraction (\(\mu\)XRD) and by SEM-EDS analysis, which also revealed abundant talc particles and few canvas fibers in the white paint (fig. 4 d). Talc was also identified by Fourier transform infrared spectroscopy (FTIR) by its absorptions at ca. 3677, 1024 and 666 cm\(^{-1}\) in samples of white paint with varying fluorescence and gloss indicating a commercial formulation of the paints\(^{15}\). In addition to these components, particles of lithopone, a pigment produced through the co-precipitation of zinc sulfide and barium sulfate, were detected by SEM-EDS in the white layer regardless of green or purple fluorescence (fig. 4 d).

The relevant elemental distribution maps obtained by macro X-ray fluorescence (MA-XRF) of two areas of the painting include white, black, and red paints and are presented in figure 5. The technique confirmed that titanium, barium, and zinc, along with relatively very small amounts of lead, are present in the white paint (fig. 5, the barium distribution map is not shown in this figure); lead was below the detection limit of SEM-EDS performed on most of the cross-section shown in figure 5, but was found in trace amounts associated with some lithopone particles.

In the area of the red disc, calcium, iron, manganese, potassium, and phosphorus were observed by MA-XRF (fig. 5, Maps Area 1). FTIR analysis of a particle of the organic red pigment in the red paint identified it as an anthraquinone-based colorant. Visual examination and the detection of phosphorus and calcium by MA-XRF indicate that a black pigment, likely a bone or ivory black, is also present in the red paint. It is noteworthy that iron and manganese are not observed in the border of the disc.

In the area of the black blast, calcium, iron, manganese, potassium, and phosphorus were observed by MA-XRF (fig. 5, Maps Area 2). Raman analysis of a black paint sample showed the presence of a carbon-based black pigment\(^{14}\). MA-XRF and SEM-EDS showed the presence of phosphorus and calcium indicating that it is a bone or ivory black\(^{15}\). FTIR confirmed the presence of bone or ivory black\(^{16}\), while hydroxyapatite was identified by \(\mu\)XRD. The detection of Fe and Mn by MA-XRF and SEM-EDS indicate that an earth pigment, possibly an umber, is present in the black paint mixture\(^{17}\).

The binder of the paints was identified as oil by FTIR\(^{18}\) and further characterized by pyrolysis gas chromatography/mass spectrometry (Py-GC/MS), with and without derivatization. Samples from four white areas of varying gloss and UV fluorescence, a sample from the red, and two samples from black areas did not contain any polyol or other cross-linking molecules, ruling out the presence of an alkyd paint\(^{19}\). The ratios of palmitic/stearic acids (P/S) for all of the paints analyzed are nearly 1.0 while the ratios of azelaic/palmitic acids (A/P) range between 0.6 and 2.3 suggesting that the binder is linseed oil; the low ratios of suberic and sebacic acids to azelaic acid (0.1 and 0.4 respectively) indicate that the oil was not pre-polymerized\(^{20}\). The fatty acid profile excludes the use of significant amounts of sunflower, safflower, rapeseed, castor, tung, or fish oils, less expensive oils that were sometimes added to linseed oil, and no marker compounds for other common additives, such as pine resin, dammar, copal, or wax, were detected.

**Condition**

The Metropolitan Museum of Art purchased *Thrust* from French & Company (New York) in 1959. Within several months of being created, the painting entered the museum’s collection and has been maintained in climate-controlled environments ever since.

In many ways, the painting is in pristine condition. The folding strainer, while marginally flexible in the long direction when handled, is structurally sound and has maintained an even tension to the canvas, which is planar. The canvas has discolored slightly but remains strong and flexible. And the paint film is wholly intact; apart from several scratches and marks that appear to be artifacts of technique, the only blemish to the surface is a subtle three-centimeter scuff that is likely the result of handling. It’s a gem, except for one disfiguring issue: a white haze that has overtaken the black and the red passages.
First observed in 1981 on the black blast as subtle traces of “a kind of efflorescence”, the 1986 condition report documents “an enormous increase of this disfiguring [haze]” (fig. 6 a-b). The haze presented on the blast as an overall layer, most prominent in areas corresponding to strainer bars. It was also populated with a series of round spots, up to ~8 mm in diameter where it had accumulated more than the surrounding areas. At the right side of the blast, there were several zones within tidelines where the haze had a mottled effect.

By 1996, the haze had become a prominent feature of the black paint, rendering it gray in color. The painting was placed in storage until 2018, when it was viewed in consideration for display. Except for areas that were treated in 1986 (discussed below) and the areas on the right side within tidelines, the haze had developed dramatically (fig. 6 a-b); it became crust-like in appearance and now covered the center of the red disc, as well (fig. 1). The red and the black paint lost their intensity, and the contrasts between them and the white background were muted. It is worth pointing out that the surface accumulation developed into a distracting haze where manganese and iron are observed in the XRF maps (fig. 5). In the red disc, the areas that contain manganese and iron have a different appearance in the UV image (fig. 3).

The surface accumulation had a variable thickness resulting in an uneven graying effect throughout the black and the red paint; artifacts from how the paint had been manipulated with the squeegee, brush, palette knife, or rag had become exaggerated.

Fig. 5. On the left side of the figure, images of the painting taken under visible (top) and UV (bottom) illumination. On the right of these images are the elemental distribution maps acquired by MA-XRF in the two areas of Thrust indicated by red (Area 1) and blue (Area 2) rectangles (see image in the top left). The maps correspond, from left to right, to: zinc (Zn), calcium (Ca), iron (Fe), lead (Pb), manganese (Mn), potassium (K), phosphorus (P) and titanium (Ti). © Adolph and Esther Gottlieb Foundation/Adagp, Paris, 2023.

Fig. 6 a-b. Before treatment photographs showing the progression of the haze from 1986 (a) to 2018 (b). The efflorescence accumulated dramatically in the black paint except for areas associated with the small round spots that appear pale in the 1986 image, because they were treated at that time, and the larger areas within the tidelines, which at present may not be explained.

Characterization of efflorescence in *Thrust*

Figure 7a-c shows photomicrographs of a sample cross-section taken from a black paint area where the surface deposit is clearly visible at the top of the stratigraphy (fig. 7c, layer 3). Conversely, the accumulation is not visible in the photomicrographs of the cross-section taken from the white paint area (fig. 4a-c), but could be detected and characterized by chemical analysis as discussed below.

Sample scrapings of the surface accumulation on the red, black, and white paints were analyzed by Raman spectroscopy, FTIR and μXRD. In all of these samples, Raman bands were observed at ca. 1061, 1128, 1293, 1437 and 1458 cm⁻¹ (the last one relatively broader), wavenumbers that are consistent with strong or very strong peaks for palmitic acid, stearic acid, and the corresponding carboxylates (soaps) of zinc and lead (fig. 7d). In our case, weaker peaks that would allow differentiating these species were below the detection limit of Raman spectroscopy, however FTIR analysis confirmed the presence of stearic and palmitic fatty acids as well as zinc and lead carboxylates. In addition to the Raman bands mentioned above, in a scraping taken from the surface of the black paint, a peak at ca. 1097 cm⁻¹ was detected while a band at 1095 cm⁻¹ was present in spectra acquired in a scraping from the surface of a white paint area. A very strong Raman band at 1093 cm⁻¹ has been reported for zinc oleate in a sample of the pure compound, along with very strong features at ca. 1061, 1295, 1438 and 1458 cm⁻¹ that overlap bands of palmitic acid, stearic acid, and the corresponding carboxylates.
Fig. 9. During treatment (2022) photographs showing the efflorescence before (right side of each photograph) and after (left side of each photograph) heating. © The Metropolitan Museum of Art/E. Read/S. Digney-Peer. © Adolph and Esther Gottlieb Foundation/Adagp, Paris, 2023.
of zinc and lead; while a medium intensity peak at 1097 cm\(^{-1}\) is present in Raman spectra of pure lead palmitate\(^{24}\). Therefore, we can conclude that both saturated fatty acids, most likely palmitic and stearic, along with lead and zinc soaps are present in and at the surface of the red, black, and white paints in *Thrust*.

Only in the FTIR spectrum acquired from a scraping of the accumulation on the black paint, a weak sharp peak at ca. 1318 cm\(^{-1}\) along with a broad feature around 1625 cm\(^{-1}\) were observed. These are frequencies reported for calcium oxalate\(^{23}\) but they overlap bands of palmitic and stearic acids at ca. 1311 and 1313 cm\(^{-1}\), respectively, and at ca. 1318 cm\(^{-1}\) for lead stearate, all of which are CH\(_2\) deformation modes\(^{26}\). The Raman spectrum of calcium oxalate monohydrate (whewellite) is characterized by a doublet at ca. 1461 and 1485 cm\(^{-1}\) while that of the calcium oxalate dihydrate (weddelite) has a strong peak at ca. 1474 cm\(^{-1}\)\(^{37}\). The whewellite peak at 1461 cm\(^{-1}\) overlaps bands assigned to palmitic acid (1463 cm\(^{-1}\)), zinc palmitate (1463 cm\(^{-1}\)), zinc stearate (1458 cm\(^{-1}\)), and lead stearate (1460 cm\(^{-1}\))\(^{28}\) and no bands at 1485 cm\(^{-1}\) were observed in the Raman spectra acquired on the samples analyzed, however it is not possible to rule out a contribution from weddelite at ca. 1475 cm\(^{-1}\) where a broad band is present in the Raman spectrum (fig. 7 d).

\(\mu\)XRD detected barium sulfate and rutile in surface scrapings from the white paint, and hydroxyapatite in the scraping from the black paint, all compounds due to the presence of pigment particles in the samples. The diffraction pattern collected from the mixture of the red paint and its surface deposit, although of low intensity, indicates the presence of succinic, palmitic and/or stearic acids. No other diffraction peaks that would help confirm the presence of additional crystalline phases were obtained, perhaps due to an overall low sample crystallinity and small sample sizes.

The composition of the surface accumulation in *Thrust* suggests that its formation involves the migration of reactive species (ions, long chain fatty acids), saponification reactions and, possibly, the migration of soaps, however it is not possible to assert what triggered the processes. Factors that would increase the mobility of species in paints include environmental conditions (e.g. high temperature and relative humidity), the composition of the paints (type of pigment and binder, the pigment to oil ratio), past conservation treatments involving organic solvents, and the artist’s working practice\(^{29}\). Other than the local interventions with solvents described in the next section, the painting has not been treated; however, as mentioned above, Gottlieb tailored his proportions of linseed oil, resins, turpentine, mineral spirits, and possibly other solvents\(^{29}\). High proportions of linseed oil in the paints will supply larger amounts of long chain saturated fatty acids, and organic solvents are known to increase the rate of fatty acid migration and metal soap formation\(^{31}\).

### Treatment

*Thrust* was first treated in 1986 in an attempt to reduce the gray appearance of the efflorescence on the black paint, which was so sensitive that dusting with a sable brush picked up pigment. It was decided at that time to leave the overall accumulation of efflorescence intact, however the prominent hazy spots (fig. 6 a-b) were reduced by dotting them with a sable brush damp with ethanol without applying pressure. With the spots no longer visible, the overall haze became far less distracting.

In order to treat the dramatic increase in the surface accumulation that occurred since 1986, cleaning tests were undertaken in 2022 with dry sable and bristle brushes. The paint film appeared to have become less sensitive to mechanical cleaning than it had been in 1986. While brushing was possible in tested areas, reducing the hazy appearance required a stiff bristle brush with an appreciable amount of pressure\(^{22}\). Given the scale of the affected area, the variable gloss, and the fact that Gottlieb modified his paint\(^{33}\), it was considered that the sensitivity of the paint could be unpredictable. Additionally, even after treatment the mobile species may continue to migrate through the paint and accumulate at the surface, necessitating further remediation throughout the life of the painting. The compounded effect of repeated interventions with a stiff bristle brush was deemed too abrasive for the paint film.

Treatment with a hot air pencil (fig. 8 and 9) was considered as a potential alternative. This technique takes advantage of the physical properties of the compounds in the efflorescence which, depending on its composition, may begin to melt at +/- 63°C\(^{14}\). When the temperature is raised to the melting points of its constituents, the haze may disappear, revealing the more saturated appearance of the artist’s paint film that lies below\(^{25}\).

The technique requires balancing numerous variables, such as nozzle size, temperature, distance to the area of interest, duration of heat exposure, fan speed, and hand motion. Temperature measuring strips were used to establish a working method that allowed the melting point to be reached in a controlled manner; too much heat risked affecting the gloss of the paint and triggering additional physical and chemical changes\(^{26}\). A narrow nozzle size of 3.0 mm was selected as it was more controllable than wider nozzles.

Heat treatment alone did not remove as much of the haze as heat treatment following brushing with a bristle brush. However, it achieved a resounding improvement. The process was straightforward at the left side of the blast; there was a consistent shift in saturation while the accumulation was heated, leaving a healthy-looking paint film with a matte surface upon cooling. Moving towards the right, the heat response of the efflorescence occurred more quickly with variable results; to keep the right side in balance with the left side, the duration of heat exposure and the distance of the pencil to the area of interest were
constantly adjusted. The variable response of the surface accumulation to the hot air pencil treatment may be due to its heterogeneous composition.

Observations during testing also suggested that the paint responded differently on the right side of the blast, where it appeared to be more sensitive to heat. Heat exposure was tightly controlled to prevent the gloss from being affected. Such variability may be attributed to uneven mixing of Gottlieb’s materials and techniques.

The overall effect of the treatment of the black blast is that of a paint film with a faintly mottled surface, which was noticeable through the haze before treatment, with a variable gloss related to Gottlieb’s materials and techniques.

The treatment was straightforward for the red disc, where the surface accumulation reacted to the heat consistently from one side to the other. Fewer residues appeared to remain after heating on the red disc than the black blast. This area did not exhibit the same sensitivity to brushing as the black paint, so residues that remained after heating were slightly reduced by locally brushing with a sable brush.

As no visible sign of an accumulation was detectable with the unaided eye or with optical magnification on the white paint, these areas were not treated.

Conclusion

Gottlieb stated: “I want to express the utmost intensity of the color, bring out the quality, make it expressive. At the same time, I would also like to bring out a certain immaterial character that it can have, so that it exists as sensation and a feeling and that it will carry nuances which are not necessarily inherent in the color, which are brought out by juxtaposition.”

The graying effect of the accumulated saturated fatty acids, lead and zinc soaps, and possibly calcium oxalate suppressed the intensity of the red disc and the black blast and undermined the nuances created by their juxtaposition. As the purpose of the painting is for the viewer’s subconscious to ascribe its own meaning to it, even slight color imbalances compromise the result that Gottlieb labored to produce and jeopardize the painting’s reason for being.

While a residual amount of the surface accumulation remained on the blast post-treatment, the intensity of the colors and the relationship between them have been re-established. Perhaps most notably, the halo, which had lost its relationship to the discolored disc, now functions to dramatic effect, making it appear to glow. For a painting whose only two shapes are flat forms, the combination of these elements, liberated from the gray veil, creates an animated and atmospheric space, charged with an intensity that is won by Gottlieb’s palette choices.

Methodology

The methodology used is described online in the Supplementary information file on OpenEdition Journal: http://journals.openedition.org/techne/16944

Acknowledgments

We would like to thank Sanford Hirsch, Executive Director, Adolph and Esther Gottlieb Foundation, for being an invaluable resource throughout the treatment of Thrust and the writing of this article. Also James Squires, Chief Conservator, and Pam Skiles, Senior Paintings Conservator, Clyfford Still Museum, for sharing their experience with using a hot air pencil to treat efflorescence. We thank our colleagues at The Metropolitan Museum of Art in the Department of Paintings Conservation under the direction of Michael Gallagher, and the Department of Scientific Research under the direction of Marco Leona, for their support throughout this work; we are especially grateful to Lucy Belloli, Paintings Conservator (retired) and Charlotte Hale, Walter Burke Conservator, for their examination and treatment of Thrust in 1986.

Notes

4. The color and shape of the disc and the blast vary from painting to painting. There may be more than one disc. Occasionally, the disc is next to or below the blast. The blast is more commonly referred to as a “burst”. As “burst” is also the title of several paintings and the term that refers to this series of paintings, “blast” will be used in this paper to describe the black form for clarity.
5. Friedman, 1962, p. 32.
6. Several “bursts” have the same dimensions as Thrust, but none are larger.
7. Friedman, 1962, p. 34.
8. As per Sanford Hirsch, Executive Director of the Adolph and Esther Gottlieb Foundation, Adolph Gottlieb worked with wood and the foldable strainer appears to be hand-made and of his creation.
9. Unpublished communication with Sanford Hirsch, Executive Director of the Adolph and Esther Gottlieb Foundation, who wrote: “Gottlieb freely chose and mixed media depending on the results he wanted. He would have jars of ‘mediums’ in his studio ready to use, and these would be his own selection of and proportions of linseed oil, turps, mineral spirits, damar, copal, and possibly other solvents or resins. As he began painting professionally in 1924, he had an extensive knowledge of what formula would get him a specific result.”
14. With characteristic broad bands at ca. 1325 and 1580 cm$^{-1}$.
15. The PO$_4^{3-}$ mode expected at ca. 960 cm$^{-1}$ for bone black (Bell et al., 1997).
was below detection in the Raman spectra acquired in the black paint sample.

16. With characteristic absorptions at ca. 1023 and 2014 cm⁻¹.

17. For the red and black areas, it is not possible to determine by MA-XRF whether some titanium, zinc, barium and lead, components of the white paint in a lower layer, are also admixed in the paint colors.

18. With absorptions at ca. 2921, 2855, 1741 (sh), 1703, 1466, and 1411 cm⁻¹.


20. For traditional artists oil paints, fatty acid ratios of palmitic (P), stearic (S), and azelaic (A) acids may be used to help determine the type of oil present. Drying oils normally have A/P ratios of ~1, while semi-drying oil and non-drying oils have an A/P of 1.

Bibliography


Unpublished documents


Supplementary information file on methodology

**Samples and optical microscopy**

Three samples taken from white paint areas and one from a black area were mounted as cross-sections in Technovit® resin, polished, examined by optical microscopy, and analyzed by Raman spectroscopy and SEM-EDS. For the microscopic examination, a Zeiss Axio Imager M2m microscope was used, with 50x, 100x, 200x, and 400x magnifications, an Axiocam HRc digital camera and AxioVision 4.X.X software. Photomicrographs of one of the samples taken from the white paint and of the sample from the black paint are presented in fig. 4 a-c and fig. 7 a-c, respectively. The other two samples from the white paint were found to have similar stratigraphy and compositions so only results on one sample are reported.

Microscopic sample scrapings were removed from the efflorescence in the red, black, and white paints. These samples were analyzed by Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). A particle of the organic red pigment in the red paint mixture was analyzed by FTIR. In addition to these samples, four microsamples of white paints of varying gloss and UV fluorescence, one red, and two black paints were removed and analyzed by GC-MS.

**Macro X-ray fluorescence (MA-XRF)**

MA-XRF analysis was performed in two areas of the painting using a Bruker M6 Jetstream® system equipped with a Rh source operating at 50kV and 600μA. The focal spot size was 580 microns, the step size was 650 microns and the dwell time was 120 ms/pixel. The spatial distributions of the elements of interest were obtained using the Bruker M6® software.

**Raman spectroscopy**

Raman spectroscopy measurements on sample scrapings and cross-sections were done using a Renishaw System 1000® coupled to a Leica DM LM microscope. Spectra were acquired using a 785 nm laser excitation focused on the samples using a 50x objective lens, with integration times of 60 s. A 1200 lines/mm grating and a thermoelectrically cooled CCD detector were used. Powers at the samples were set at 2.5mW using neutral density filters.

**Fourier transform infrared spectroscopy (FTIR)**

FTIR analysis was performed with a Bruker Hyperion 3000 FTIR spectrometer equipped with a mercury cadmium telluride (MCT) detector. The samples were mounted in a Spectra Tech diamond anvil cell and analyzed through a 15xobjective in transmission mode. Spectra were collected with a 4 cm⁻¹ resolution and were obtained as the sum of 256 scans. Spectra were interpreted by comparison with the NIST 2007 library and personal databases as well as published literature.

**Pyrolysis gas chromatography/Mass spectrometry (Py-GC/MS)**

Py-GC/MS analysis was carried out on an Agilent 8890 GC, 5977B MSD and a Frontier lab Double-Shot 3030D pyrolyzer (no autosampler) as described in Pozzi et al. with the following changes: Samples (~30 micrograms) were pyrolyzed at 550°C for 20 s without and with derivatization using tetramethylammonium hydroxide (TMAH; 2 mL of 25% in methanol (Fisher Scientific)) and injected on the column with a 20:1 or 10:1 split, in accordance with the medium content. The GC oven temperature program was held at 320°C for 15 min after the gradient. Data analysis was performed on an Agilent MSD ChemStation F.01.03.2357 software by comparison with the NIST 2017 spectral libraries.

**SEM-EDS**

SEM-EDS analyses were performed on scrapings and the carbon-coated cross-sections with a FE-SEM Zeiss Sigma HD, equipped with an Oxford Instrument X-Max® 80 SDD detector. Backscattered electron (BSE) images, energy-dispersive spectrometry (EDS) analysis, and X-ray mapping were carried out with an accelerating voltage of 20kV in high vacuum.

**Micro X-ray diffraction**

µXRD analysis of sample scrapings was performed with a Bruker D8 Advance instrument using Cu Kα radiation at 40kV and 40 mA. The diffractometer is equipped with a Göbel mirror, a 1mm UBC collimator, and an Eiger2R 500k Hybrid Photon Counting detector working in 2D mode. Continuous scans were collected between 10° and 60° 2θ, with a step size of 0.02° and a time step between 0.5 s and 1 s. Micro-samples were mounted on a rotating low-background plate.