

Spectroscopic Studies on the Darkening of Lead White

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Lead white is an historically important paint used by artists since antiquity. The darkening of lead white has been well documented in works of art such as paintings. In this paper, mid-infrared (MIR) and visible spectroscopy were used to examine spectral changes accompanying the darkening of lead white paint as a result of exposure to H₂S(g). Laboratory-prepared paint and a commercial lead white paint were used to observe the darkening reaction over time. Structural changes to the pigment, 2PbCO₃·Pb(OH)₂, in lead white were readily detected using MIR by applying a thin film on a KBr pellet. Spectral changes at 3541 (O–H stretch), 1400 (C–O), and 680 cm⁻¹ (C–O) were the most significant over time as the paint darkened. Visible spectra were also collected to provide a semi-quantitative measure of color change with structural changes observed by MIR. Experiments in the visible region were also conducted to compare the spectral response as % reflected and % transmitted light as lead white darkened. The effect of different binding agents (egg tempera, linseed oil, water, and gum Arabic) on the rate of darkening of lead white was also examined. Other sulfur-containing pigments such as orpiment and realgar were also tested for their ability to darken lead white. By applying paint as a thin film inside a sealed cuvette, darkening of lead white was observed in the visible spectra (800 nm) when either powdered orpiment or realgar was in placed in the cuvette for 24 h.

Index Headings: Lead white; Paint degradation; Infrared and visible spectroscopy; Pigments; Paint.

INTRODUCTION

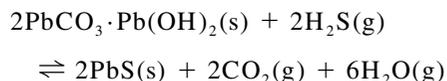
The change in appearance of paint over time is a well-known process that has affected historically significant works of art. Change in the appearance of painted surfaces can be the result of the formation of a compound on the paint surface that is different in color from that of the original or it can be due to fading or darkening. Darkening is often easily visible to the naked eye and can have a profoundly negative impact on the value and possibly on the interpretation of the painted object. A darkened appearance over time is one of the most common symptoms of aging of painted surfaces. Darkening can be a result of many processes including the photochemical yellowing of a varnish coating and photochemical reactions or chemical reactions with the pigment or the binding agent.

Lead white (also known as flake white) has been described as the most important white paint prior to the commercial development of ZnO and TiO₂ as white pigments.¹ Lead white was the single most important white paint used in European easel painting until well into the 19th century.^{1,2} The pigment used in this paint is basic lead(II) carbonate, 2Pb(CO₃)·Pb(OH)₂. It has been used

with a variety of binding agents including water, linseed oil, gum Arabic, egg tempera, and animal glue.² Because of its widespread use by painters, lead white has received the attention of conservation scientists and spectroscopists as evidenced by the number of papers describing its spectral and physical properties. In separate studies,^{3–5} the use of lead white (tempera) as a test paint for dosimeters has been described to monitor the degree of chemical change in museums for the purpose of environmental indoor monitoring.

The use of mid-infrared (MIR) spectroscopy has been described for identifying a number of pigments in paint fragments including lead white.⁶ Laser-induced breakdown spectroscopy has been successfully used for identifying lead(II) carbonate on an illuminated manuscript that dated from the 12–13th century A.D.⁷ Raman spectroscopy is also well suited as a spectroscopic technique for identifying most pigments used by artists, including lead white.⁸ Two separate Raman spectroscopic libraries have been published in the last decade that illustrate the usefulness of this spectroscopic technique.^{9,10} Clark et al. used Raman spectroscopy to detect a white pigment on a rare 13th century manuscript that had degraded significantly.^{11–13} These authors detected lead white, and in darkened areas, they were able to identify PbS. Interestingly, other pigments identified on the manuscript also included a number of sulfide-containing pigments such as vermilion (HgS), orpiment (As₂S₃), realgar (α-As₄S₄), and pararealgar (β-As₄S₄).

The permanence of lead white has been questioned because it is known to darken in many works of art over time. The darkening of lead white has been attributed to the presence of H₂S(g), which reacts with 2PbCO₃·Pb(OH)₂, resulting in the formation of PbS according to the reaction:



A number of studies have been carried out on the darkening of lead white. For example, Carlyle and Townsend¹⁴ have investigated the formation of PbS as a cause for darkening of 19th century painting materials. Work by Norville-Day and Townsend¹⁵ has shown that the formation of PbS as a result of exposure to H₂S is limited to the surface (less than 1 μm) of the paint layer. More recently, Smith and Clark¹⁶ have investigated the blackening of a number of important pigments including basic lead(II) carbonate using Raman spectroscopy.

Historically, one of the most important causes of H₂S(g) exposure to paintings could be the burning of coal and possibly gas lighting.² It has also been suggested that

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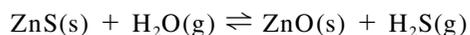
microbial activity¹⁷ could be a source of H₂S. Specific types of bacteria are capable of producing H₂S in oxygen-poor environments and therefore utilize sulfur in their metabolic pathways. This environment is possible beneath a varnished surface where bacteria may be encapsulated in an oxygen-poor environment. Binding compounds in paint such as egg yolk or oil should be able to provide the required sulfur for H₂S production.

While some work has been published on the blackening of basic lead carbonate and lead carbonate,¹⁵ little work has been done to duplicate the darkening process of lead white in laboratory-prepared paint samples, which contain binding agents. Apart from damaging potential valuable artwork, the advantage of using laboratory-prepared paint samples is the additional control over the amount of binding agent and pigment, which is not possible with commercially available paint. Modern commercially available paint may also contain drying agents and additives, which can make these paints difficult to compare with traditional ones prepared by the artist. The objective of this study was to use a variety of techniques to examine chemical and spectroscopic properties of the darkening of lead white using laboratory-prepared paints (i.e., with binding agents) and a commercially available paint.

EXPERIMENTAL

Paint Preparation. Laboratory-prepared paint consisted of basic lead(II) carbonate (Aldrich) mixed with various binders (linseed oil, gum Arabic, water, egg tempera). Initially, a paste was prepared by adding water to the pigment in an approximate ratio of 5:1 (lead(II) carbonate to water). Small amounts of binding agent were added to the paste until the paint was of a consistency that could be easily spread onto a surface. In the case of egg tempera, only the egg yolk was used as the binding agent in the preparation.¹⁸ A commercial lead white paint (Grumbacher) that had linseed oil as a binding agent was also used. Thin films of paint were dry in less than 1 h after their application to the surface of a KBr pellet or plastic cuvette.

Darkening Process. The darkening of lead white via reaction with H₂S(g) was achieved by placing a small amount of ZnS(s) in a sealed vessel containing the paint samples. Zinc sulfide reacts with moisture in the air to form H₂S(g) according to the reaction:



The advantages of using ZnS are that it is inexpensive, relatively nontoxic, and reacts slowly (0–24 h) enough with air to allow easy handling for these experiments. Generating H₂S(g) by this approach is both economical and practical as no equipment such as gas tanks or regulators for the H₂S was necessary and only small amounts of gas were required for each experiment.

Fourier Transform Infrared Spectroscopy. Fourier transform MIR spectra of the paint samples were obtained using a Bomem Hartmann & Braun MB Series IR spectrometer. For each spectrum, the % transmittance was recorded over the range of 300–4000 cm⁻¹ using an average of 16 scans and a resolution of 4 cm⁻¹. A thin film of paint was applied to the surface of a KBr pellet and

then left to dry. In order to sample the paint at the same location over time, a sample holder for the KBr pellet was constructed. Each KBr pellet was mounted onto a 35-mm film slide frame, which could be placed directly into the spectrometer. A hole for the pellet was cut out of aluminum tape, slightly smaller in size than the pellet itself, and used to mount the pellet to the film slide.

Infrared spectra of each paint sample were obtained at specific time intervals after exposure to H₂S(g) over 24–60 h. Each paint sample was placed into a 250 mL beaker, along with two small polystyrene sampling beakers, one containing 500 mg of zinc sulfide (Aldrich) and the other containing 100 μL of deionized water. The painted side of the KBr pellet was positioned facing the zinc sulfide and water. Parafilm was used to seal the beaker. An unpainted KBr pellet was scanned as the background spectrum.

Fiber-Optic Visible Spectrometry. Corresponding visible spectra of the painted KBr pellets were obtained using a Model SD2000-TR Ocean Optics Miniature Fiber Optic Spectrometer with an SAD500-S A/D converter. A white certified reflectance standard (Labsphere) was used and the fiber-optic probe was clamped into position at a height from the standard that resulted in the maximum signal. Each painted KBr pellet was placed under the probe on top of a nonreflecting black surface at the same height as the standard. Care was taken to sample the same relative position and height of the paint surface. The % reflectance over the range 400–800 nm with a resolution of 0.5 nm was recorded.

Visible Spectrophotometry. A Shimadzu UV-2501PC spectrophotometer was used to record the absorbance and % transmittance of the paint samples at 400–800 nm with a slit width of 2.0 nm over time. A thin film of paint was applied to the inside wall of a plastic cuvette (pathlength = 10 mm) and left to dry. The initial absorbance of the paint was obtained followed by the addition of 50 mg of ZnS and 10 μL of H₂O to the cuvette before sealing with parafilm. Absorbance was automatically obtained every 15 min for 24 h or until the absorbance leveled off. A Julabo F12 water bath was connected to the spectrophotometer for temperature control (20, 30, and 50 °C) of the cuvettes. Cuvettes were also used with realgar and orpiment in place of ZnS to test their ability to darken lead white. In one set of cuvettes, the one wall adjacent to the Flake White was painted with a paste made with either realgar or orpiment (5:1 ratio of pigment to water). Additional realgar or orpiment was placed at the bottom of the cuvette to bring the amount added to about 50 mg. In another set of cuvettes, the pigments realgar and orpiment were brought into contact with the lead(II) carbonate. Approximately equal amounts of pigment and lead(II) carbonate were mixed in the preparation of the paste followed by the addition of the binder. This paint, containing a mixture of lead(II) carbonate and either realgar or orpiment, was applied to the inside wall of a cuvette. All cuvettes contained 10 μL of H₂O and were sealed with parafilm.

RESULTS AND DISCUSSION

The darkening of lead white paint is readily monitored in the MIR by painting a thin film on a KBr pellet. Prac-

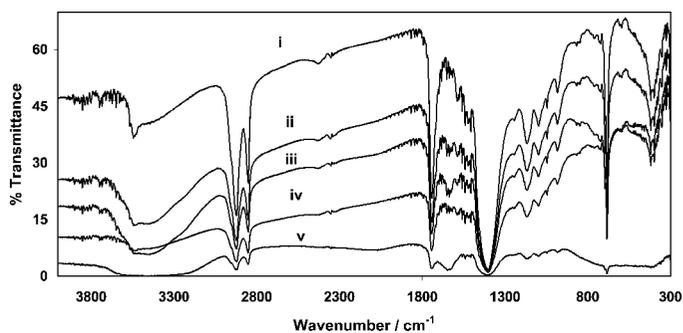


FIG. 1. Change in MIR transmittance of a commercial lead white (basic lead(II) carbonate in linseed oil) after exposure to H_2S for: (i) 0 h, (ii) 2 h, (iii) 4 h, (iv) 12 h, and (v) 24 h.

tical considerations for this approach include minimizing water (if possible) and making the KBr pellet thick enough to allow handling and mounting on a 35-mm film slide frame. Mounting KBr pellets in this manner made it possible to follow the darkening process over long periods of time (>24 h) and ensured that the same location was monitored throughout. This was critical because even small changes in location seriously affected the transmission of radiation through the paint film. Spectral properties of pure lead white paint are usually dominated by the presence of the pigment rather than the binding agent since the mass of pigment is at least 8–9 fold higher than that of the binding agent. The MIR spectra of the pigment, basic lead(II) carbonate, used in lead white can be found in the literature¹ and will not be duplicated here. Assignments of the relevant peaks associated with the basic lead(II) carbonate are: 3541 cm^{-1} due to O–H stretch, $Pb(OH)_2$; 1400 cm^{-1} due to antisymmetric C–O stretch of CO_3 ; 1046 cm^{-1} due to symmetric C–O stretch, CO_3 ; and 680 cm^{-1} due to C–O rocking deformation, CO_3 . Other peaks (e.g., 3000 cm^{-1}) can be attributed to hydrocarbons (C–H stretch) in the binding agent.¹

One goal of this work was to correlate structural changes using MIR spectroscopy with the darkening of lead white paint over time. This experiment was carried out using laboratory-prepared paint consisting of basic lead carbonate mixed with different binding media (oil, water, gum, egg tempera) as well as a commercially available lead white paint. Figure 1 (spectra i–v) shows the changes in the MIR spectra of a thin film of lead white paint over time after exposure to $H_2S(g)$ from the decomposition of ZnS. As lead white paint darkens, the disappearance of three peaks at 3540 , 1400 , and 680 cm^{-1} is clearly evident. The disappearance of C–O is evidenced by the decreased transmittance at 1400 and 680 cm^{-1} . Figure 2 shows more clearly the change in the C–O stretch at 1400 cm^{-1} as the C–O group bonded to Pb is replaced with the sulfide. While the absorbance at 1400 cm^{-1} is quite broad relative to the absorbance at 680 cm^{-1} , both peaks appear to be equally useful for measuring the darkening reaction of lead carbonate with H_2S . Decreased transmittance at 3540 cm^{-1} is also observed as a result of the disappearance of O–H. The difficulty in using MIR for monitoring O–H is that trace amounts of water can seriously affect the intensity of this peak. This would be even more problematic if the darkening process is monitored using MIR reflectance.

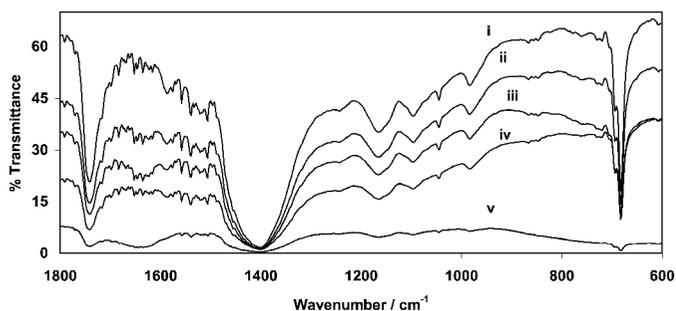


FIG. 2. Change in the carbonyl region of IR transmittance of a commercial lead white (basic lead(II) carbonate in linseed oil) after exposure to H_2S for: (i) 0 h, (ii) 2 h, (iii) 4 h, (iv) 12 h, and (v) 24 h.

The disappearance of two different functional groups confirms that two different lead atoms are susceptible to formation of PbS by the H_2S . One study¹⁵ suggested that the Pb atoms bonded to OH may be more reactive toward H_2S , which is a weak acid, than the Pb atoms bonded to carbonate. Furthermore, it should be expected that mixed oxides can form; however, the MIR was not useful for detecting their formation.

The darkening process is essentially complete after approximately 24 h. Another spectral feature of the darkening process is decreased % transmittance at all wavelengths in the MIR. This should be expected because the darkened surface absorbs more of the source radiation at all visible and IR wavelengths. Because of the similarity in the MIR spectra of the darkening of lead(II) carbonate in different binders, only the darkening of the commercial lead white is shown in Fig. 1. While MIR is useful for monitoring the darkening reaction, its usefulness in detecting the degradation products such as PbS or PbO and PbO_2 is not possible. Other spectroscopic techniques such as Raman spectroscopy^{15,19} have been shown to be quite suitable for sensitive detection of compounds such as PbS .

In order to compare changes in the visible spectra with the structural changes observed in the MIR, visible spectra of paint samples were also collected using a fiber-optic visible spectrophotometer in reflectance mode. Figure 3 shows near simultaneous change in the visible spectra as the lead white darkened with respect to time. Change in the visible spectra was measured by placing the fiber-optic probe above the KBr pellet containing lead

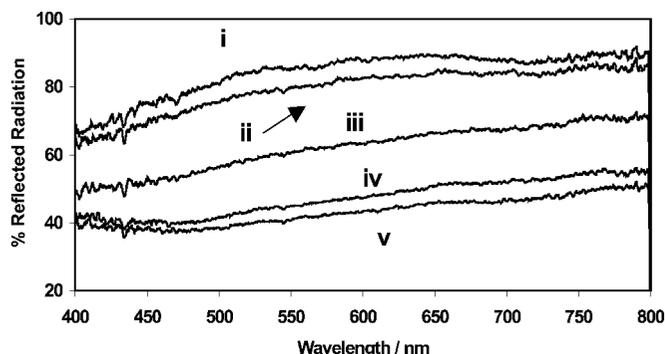


FIG. 3. Corresponding change in % reflected visible light from a commercial lead white (basic lead(II) carbonate in linseed oil) after exposure to H_2S for: (i) 2 h, (ii) 4 h, (iii) 12 h, and (iv) 24 h.

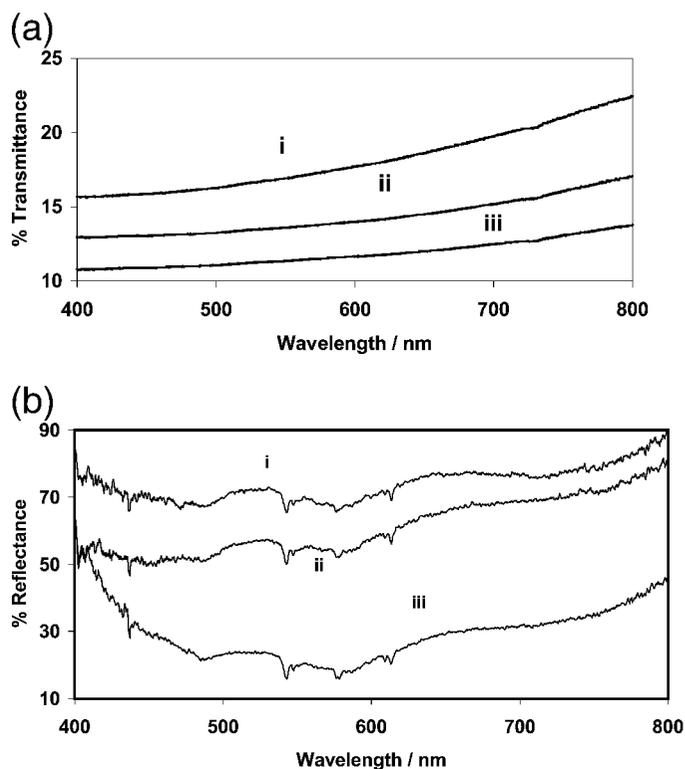


FIG. 4. Darkening of a commercial lead white in the visible region at (i) $t = 0$ h, (ii) $t = 2$ h, and (iii) $t = 24$ h as monitored by (a) % transmission and (b) % reflectance (fiber optic).

white prior to collecting the MIR spectra. In this manner, visual effects can be semi-quantitatively correlated with the structural changes in the MIR. The change in % reflected visible light was greater than the change in % transmitted IR light.

Using the data collected in Fig. 1, peak height ratios (calculated using absorbance data) were measured during the darkening process to determine if there was any correlation between peak height ratios and the degree of darkening on the paint surface over time. The low intensity O-H peak at 3500 cm^{-1} and the presence of water in the KBr seriously affected the peak height. It is difficult to prove conclusively if there is a direct relationship between peak heights and the degree of darkening of the flake white. An interesting potential application of these observations would be to use peak height ratios for evaluating the degree of exposure of lead white to H_2S . It is possible that MIR reflectance spectra on an actual painting would not give useful results since light scattering and the presence of dust or dirt could affect the peak ratios.

One aspect of monitoring the darkening process is the apparent nonlinearity of the spectral change (both IR and visible) as a function of time. This may be expected, since the formation of H_2S from the decomposition of ZnS was probably not linear with respect to time and its concentration should be increasing in the sealed container. Secondly, it appeared visually that the darkening process was essentially complete well before the MIR spectra indicated that it was. This is likely because visually, only surface phenomena are observed in reflectance

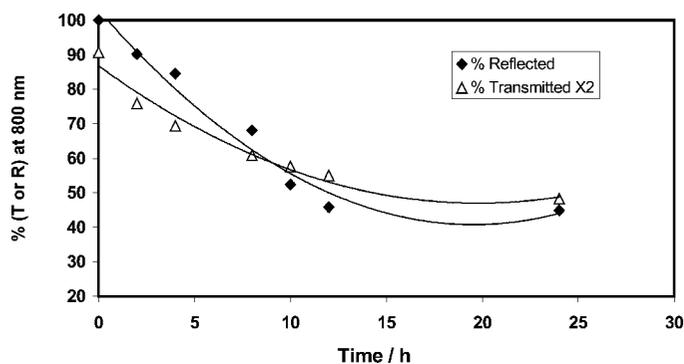


FIG. 5. Change in % transmittance and % reflectance at 800 nm during the darkening of lead white.

mode, whereas the MIR spectra in transmission mode detect structural change throughout the thin film.

Measurements of darkening of lead white were also performed in a sealed cuvette and monitored using a visible spectrophotometer. Paint was applied as a thin film to the inside of a sealed cuvette, which allowed light to pass through it. The change in spectra, collected as % transmittance, is shown in Fig. 4a. For comparison the change in spectra as % reflectance using a fiber-optic probe is shown in Fig. 4b. It is worth noting that % reflectance spectra are not as affected by the paint thickness as % transmittance spectra in the visible spectrum. Using the same data, the % transmitted and % reflected light at 800 nm were plotted in Fig. 5. The data shown in Figs. 4 and 5 illustrate how much more sensitive the change in % reflectance is compared to that in % transmittance. This may also explain why changes in appearance seem to be apparent to the eye prior to the detection of structural changes that are detected using MIR.

To examine the role of the binding agent on the rate of darkening of lead white paint, a series of paint films with different binding agents (egg tempera, linseed oil, water, gum Arabic) was prepared and painted on the inside of different cuvettes. The paint films were then exposed to $\text{H}_2\text{S}(\text{g})$ from the decomposition of ZnS over time. As much as possible, paint films of the same thickness were applied and the same amount (10 mg) of ZnS was added to the sealed cuvette with $10\ \mu\text{L}$ of H_2O to provide humidity. The MIR spectra did not indicate anything other than expected decreases in peak intensities (e.g., C-O stretch 1400 cm^{-1}). The commercial lead white and the laboratory-prepared lead white (linseed oil) appeared to darken at a rate very similar to the laboratory-prepared oil paint. Some differences in the rate of darkening were observed depending on the binding agent that was used. The chemical matrix of both egg yolk and tempera is considerably more complex than oil or water so it is entirely possible that a different chemical or physical process (i.e., further drying) may be occurring with these binding agents. Differences in the rate of darkening may also be partially explained in terms of the amount of pigment in the light path of the spectrophotometer and the heterogeneity of the laboratory-prepared paint film.

Experiments were also conducted on the darkening of lead white paint to determine if there was any significant difference in the darkening process at elevated temperatures. This type of experiment was useful for testing

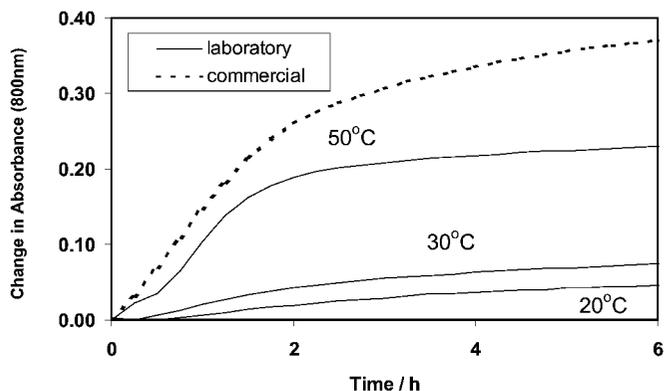


FIG. 6. Change in absorbance at 800 nm of lead white with respect to time at elevated temperature for (—) laboratory-prepared paint (linseed oil) and (---) commercially available oil paint (50 °C only).

whether the laboratory-prepared paint behaved in a manner similar to a commercial paint. The darkening of a commercial lead white paint (oil) and a laboratory-prepared lead white paint at different temperatures is illustrated in Fig. 6. It is worth noting that the commercial paint behaved in a manner similar to the laboratory-prepared paint. For the sake of clarity, only the change in absorbance is shown at 50 °C for the commercially available paint. This experiment also illustrates how elevated temperatures can dramatically accelerate the darkening process. When the darkening reaction is carried out at 20 °C, the reaction is complete after 24 h; however, at 50 °C, the reaction is essentially complete after 2 h. Modern museums can certainly deal with elevated temperature and humidity; however, for improperly stored artwork or wall paintings that are not located in a controlled environment, the potential for damage is significant.

A final series of experiments were conducted to determine if other pigments were capable of darkening lead white by a mechanism similar to the decomposition of ZnS. A number of S-containing pigments were tested by placing them in a sealed cuvette containing lead white paint. It has been shown by a number of researchers and conservation scientists that the darkening of lead white may also be due to the presence of S-containing pigments.² Examples of S-containing pigments include vermilion or cinnabar (HgS), which is a red pigment that was used to produce a flesh-colored appearance on canvas when mixed with lead white.¹ Orpiment (As₂S₃) is a yellow-colored pigment and realgar (As₄S₄) is described as an orange-yellow pigment. There are some notable examples of their usage in paintings such as Raphael's "Sistine Madonna" and da Vinci's "Last Supper" wall painting.²⁰ Therefore, it was these S-containing pigments as well as CdS and lazurite that were examined for their capability to darken lead white paint. In these experiments, lead white paint was applied as a thin film to the interior of the cuvette and the S-containing pigments were added to the cuvette as paint in two different configurations. In one set of experiments, the S-containing paint was in the same cuvette but not in contact (non-contact) with the lead white. In a second set of experiments the S-containing pigment was mixed with the wet lead white (contact) paint prior to its application on the cuvette wall. A series of paints were prepared to deter-

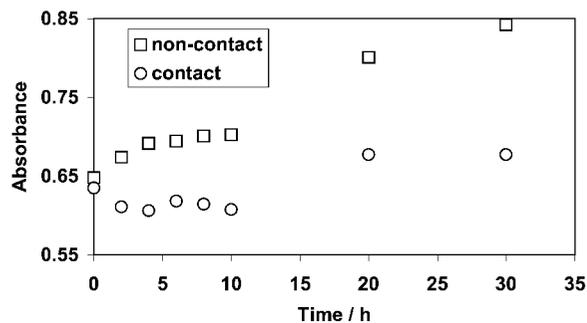


FIG. 7. Change in absorbance at 400 nm of lead white (egg tempera) with respect to time in the presence of orpiment.

mine qualitatively whether the binding agent had any noticeable effect on the darkening reaction. Visible reflectance spectra were recorded over time for lead white with various binding agents (water, linseed oil, gum Arabic, and commercial paint) that were exposed to each of the S-containing pigments.

Under these experimental conditions, only orpiment and realgar darkened lead white significantly, and the darkening was visibly noticeable to the naked eye after 24 h. Figure 7 gives an indication of the extent of darkening of lead white (egg tempera) over time due to the presence of orpiment. Though not shown, realgar gave spectral changes very similar to orpiment, which should be expected since these two pigments are chemically similar. The change in % transmittance at 400 nm was much slower when using As₂S₃ or As₄S₄ than ZnS, indicating a much slower evolution of H₂S in the cuvette. Similar changes in the spectra were evident for all wavelengths in the visible region; however, only changes at 400 nm are shown here. Initially it was hypothesized that the darkening reaction should be much quicker if the S-containing pigment was mixed with lead white (contact); however, this was not observed. Only slight darkening of lead white occurred under these conditions after 24 h with realgar and orpiment. This may be due to the encapsulation of the pigment particles in the binding matrix, which may have decreased the rate formation of H₂S(g) from the degradation of orpiment or realgar. This is not to suggest that darkening of lead white will never occur; however, the time scale is on the order of days rather than hours, as we have shown in the laboratory. It should also be noted that these experiments were carried out in the darkness of the UV-visible spectrophotometer, which prevented possible photochemical reactions. None of the other S-containing pigments darkened lead white under these conditions. The IR spectra collected (not shown) on KBr pellets were also identical in appearance to those collected for the darkening process using ZnS, indicating that the darkening mechanism is likely to be the same.

CONCLUSION

In terms of darkening, the behavior of a laboratory-prepared lead white using linseed oil as a binding agent was spectroscopically identical to that of the commercial lead white. It is unclear if the darkening of lead white can be attributed only to the presence of other pigments or the presence of H₂S in the atmosphere. In some cases, the presence of certain S-containing pigments is all that

is required to affect the appearance of lead white. This work has shown that mixing of incompatible pigments is not required for the formation of PbS. Degradation of a pigment that is physically separated from basic lead carbonate can cause the formation of PbS. Furthermore, mixing pigments within the same binding agent also does not guarantee a darkening appearance of lead carbonate. This strongly suggests that the binding agent can also play a role in preventing the formation of H₂S(g), as well as possibly protecting the lead carbonate. Another aspect worth further exploration is the effect of H₂S(g) concentration on the rate of darkening of lead white. Establishing rate constants and the order of this reaction should also provide insight into the physical aspects of the darkening process, as well as the role of parameters such as relative humidity.

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