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An Examination of Lead White Discoloration and the Impact of Treatment on Paper Artifacts: A Summary of Experimental Testing

ABSTRACT

Lead white (basic lead carbonate), a pigment used over many centuries in both European and Asian art-making traditions, has long been observed to discolor over time. Though often described as blackening, the deterioration of lead white pigment takes many different forms, with colors ranging from light pink to brown and speckled gray to black. In European works on paper, the conversion of darkened lead white (lead sulfide) to a more stable white pigment (lead sulfate), via an oxidation process, was utilized as early as 1890. The development of innovative treatment methods has been ongoing in the field of conservation, receiving impetus in recent years with the introduction of the use of peroxide gels to restore the whiteness of darkened lead white on paper artifacts. Though recent practice has seen a shift towards the use of aqueous treatment methods over the traditional application of an ethereal hydrogen peroxide solution, research on the impact of conversion treatments on paper artifacts is scarce. Presented is a summary of observations relating to the effect of various treatment methods on experimental samples. Methods examined include brush, vapor, and gel application techniques using aqueous hydrogen peroxide solutions and local brush application of an ethereal hydrogen peroxide solution.

INTRODUCTION

Darkened lead white can be one of the more distracting forms of discoloration on works of art on paper, particularly where lead white was used for heightening. The darkening of this once bright white contributes to an often severe visual imbalance and detracts from the aesthetic harmony of the image. Decision-making with regard to

treatment approach often involves collaboration between conservator and curator, or custodian. Such treatments, carried out with the intent of restoring the visual integrity of an object, raise many conservation issues: practical, aesthetic, and ethical.

Today in conservation practice, the treatment of discolored lead white refers to the oxidation of lead sulfide using the free oxygen generated by hydrogen peroxide, thereby converting it to a new white material, lead sulfate. Conservators have discussed the respective ease or difficulty of successfully carrying out the conversion process. In "The Reversion of Blackened Lead White on Paper," Daniels and Thickett (1992) refer to an unidentified, amorphous, gray discoloration that could not be fully whitened under experimental lab conditions. Wächter, in his 1975 book on conservation, reports that if only the surface of the lead white paint application is converted, the underlying pigment may continue to discolor. Further complicating the decision-making process in view of conservation treatment is the variety and variable sensitivity of paper substrates and associated media.

This article focuses on a set of experimental tests designed to investigate the impact of various treatment methods on discolored lead white. Selection of treatment methods was based on current practice as informed by a recent survey of practicing conservators¹ as well as conservation literature. The selected methods are intended to invoke a comparison of past and present and to look to the future by evaluating less practiced, but reportedly successful methods.² The changes that result from various treatment methods are evaluated and characterized through observation and the use of scanning electron microscopy (SEM).

SUMMARY OF EXPERIMENTAL TESTING

Selected Treatment Methods³

- 3% aqueous hydrogen peroxide, brush-applied
- 3% aqueous hydrogen peroxide, vapor⁴

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- <3% aqueous hydrogen peroxide, gel
- 30% hydrogen peroxide (1:1 in diethyl ether), brush-applied

Solution Preparation

The 3% aqueous solution was diluted from a 30% hydrogen peroxide solution using deionized water conditioned with calcium hydroxide. The final pH of the 3% solution was adjusted to 9 with the addition of ammonium hydroxide. For the gel technique, this 3% solution was added to a pre-mixed low-viscosity methylcellulose.⁵ The ethereal hydrogen peroxide solution was prepared by mixing equal proportions of 30% H₂O₂ with diethyl ether.⁶

Sample Preparation

Lead white pigment in a gum arabic binder was applied by brush to Whatman filter paper. Discoloration of the lead white paint was induced in a chamber by exposure to hydrogen sulfide gas. Individual test samples were derived from a single sample to ensure that each showed a paint application that was as similar as possible from one to the next and to allow more consistent observations when making comparisons related to treatment method.

An attempt was made to replicate an actual conservation treatment scenario when treating the individual samples. With the exception of the vapor technique, all treatments were executed under magnification with the aid of a stereomicroscope. Samples were carefully monitored throughout the treatment process and treatment was halted at any sign of deleterious effect to the paint layer.

EVALUATION OF SAMPLES

Factors that define a successful conversion treatment:

- achievement of a color close to the original (white)
- no discernable alteration in the pigment/paint layer
- no undesirable visual imbalance after treatment
- no adverse effect to the paper substrate (not part of this study)

Visual examination with the aid of magnification before, during, and after treatment is the method typically employed by paper conservators when evaluating a lead white conversion treatment; the above-listed conditions are contributing factors by which one gauges the degree of success. These factors take into account aesthetic considerations as well as physical changes that result from treatment intervention.

For the purposes of this study, scanning electron microscopy (SEM) was selected as an imaging method to supplement standard tools of evaluation, providing images of treated paint films with greater informational value than those captured through a standard stereomicroscope.

Vocabulary for characterization of SEM images:

- surface topography
- porosity
- particle agglomeration

Sample characterization is based on physical changes that resulted from various treatment methods as observed in the SEM images and is supported by the use of a consistent vocabulary to facilitate an equitable comparison between samples.

DURING TREATMENT OBSERVATIONS

Brush application of an aqueous solution of 3% hydrogen peroxide: Uneven conversion and binder solubility were observed. Repeated applications of the hydrogen peroxide solution were necessary to achieve color reversion, ultimately leading to pigment disruption.

Vapor application of an aqueous solution of 3% hydrogen peroxide: Incomplete, but uniform, conversion was observed. (The paint layer in the treated sample appeared gray.) Extended moisture and hydrogen peroxide exposure may be of concern, particularly to paper substrate and other media.

Gel method, <3% hydrogen peroxide: Rapid and complete conversion occurred. Concern with fully clearing gel residues remains.

Brush application of 1:1 hydrogen peroxide and ether: Rapid and complete conversion was again observed with the ethereal hydrogen peroxide solution; however, rupture of the paint layer sometimes occurred upon evaporation of the solvent.

EVALUATION OF SEM IMAGES

Brush application of an aqueous solution of 3% hydrogen peroxide: The greatest topographical change occurred with this technique, evident as distinguishable peaks and valleys. This is not completely unexpected as some binder solubility and pigment manipulation were observed during treatment. Some change in porosity is observed; the small dark pits that were visible before treatment (fig. 1), now appear as complex crevices. Agglomeration of pigment particles is frequent, with upward lifting contributing to the prominent appearance of these clumped particles on the surface (fig. 2).

Vapor application of an aqueous solution of 3% hydrogen peroxide: The Gore-Tex vapor-treated sample shows a fairly uniform surface with little topographical change, and appears most similar to the untreated sample; however, the pits are slightly larger, a feature perhaps attributable to moisture moving through the paint layer during treatment. Distribution of pigment particles across the surface appears consistent with the untreated sample (fig. 3).

Gel method, <3% hydrogen peroxide: The most uniform surface with the least amount of topographical variation is displayed in the peroxide gel sample. The size and fre-

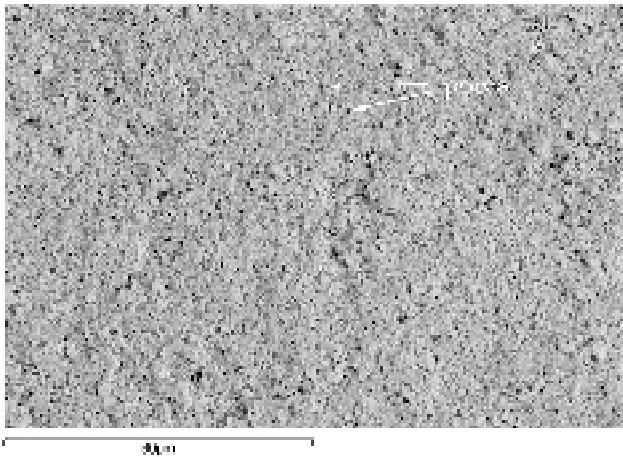


Fig. 1. Untreated sample. 1000x magnification (SEM). Dark spots are pores in the paint film.

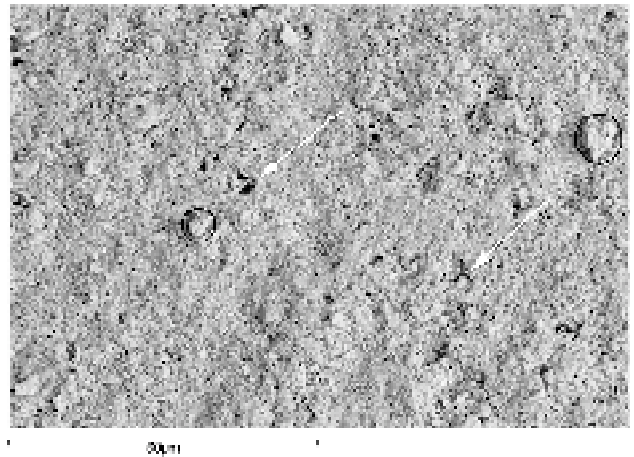


Fig. 2. Treated sample. Brush, 3% hydrogen peroxide, aq. 1000x magnification (SEM). Circled areas show particle agglomeration. Arrows point to complex pores.

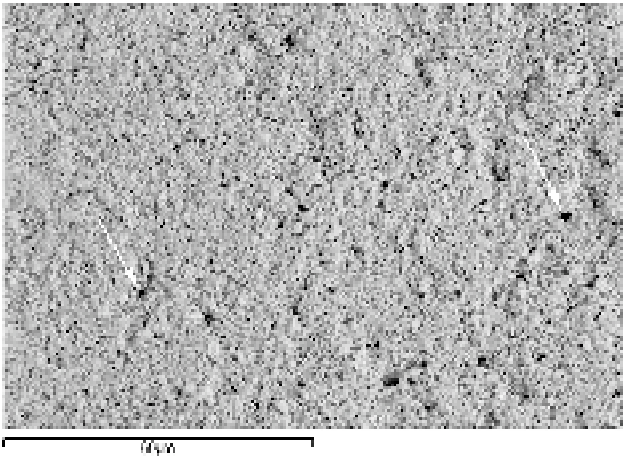


Fig. 3. Treated sample. Vapor, 3% hydrogen peroxide, aq. 1000x magnification (SEM). Arrows point to enlarged pores.

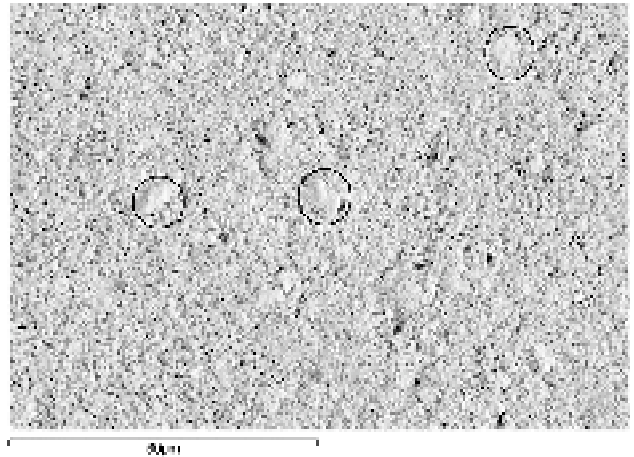


Fig. 4. Treated sample. Gel, <3% hydrogen peroxide, aq. 1000x magnification (SEM). Circled areas show particle agglomeration.

quency of pores in the paint layer appear comparable to the untreated sample. The surface appears more compact overall, a feature that may result from residual methyl cellulose effectively “consolidating” the paint layer. Agglomeration of pigment particles is observed in this sample, though the clumps remain in the same plane as surrounding pigment (fig. 4).

Brush application of 1:1 30% hydrogen peroxide and ether: In the sample treated with ethereal hydrogen peroxide extremes of treatment outcome are observed. In the successfully treated areas the surface is relatively uniform with minimal topographical variation, although [circled] areas may show signs of physical alteration. In addition, the paint layer appears less porous than in the untreated sample. The ether may play some role in closing existing pores in the paint layer by moving pigment particles as the solution quickly volatilizes from the surface. Similarly, the lack

of particle agglomeration may be attributed to the poor solubility of the gum arabic binder in the ether (fig. 5).

In the ruptured areas, the paint film is unacceptably altered. While the nature of the sample preparation and thickness of the paint film may have contributed to rupturing, artists’ materials are variable and one cannot discount the possibility of such an occurrence on an area of applied heightening with an impasto quality (fig. 6).

CONCLUSION

Every object presents unique condition issues and treatment challenges due to individual history as well as the unpredictability of artists’ materials. The goal of this project and the presented results are not intended to advocate a particular approach to treatment, but to offer observations that may be useful in facilitating an informed

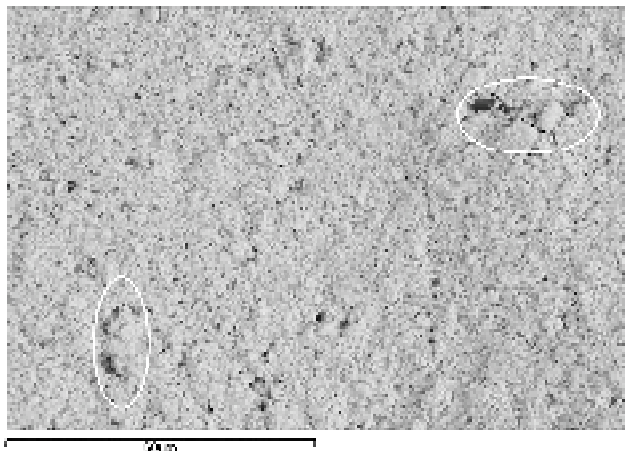


Fig. 5. Treated sample. Brush, 1:1 30% hydrogen peroxide and ether. 1000x magnification (SEM). Circled areas show possible physical alteration.

decision. Ideally, this preliminary study will encourage dialogue and future research with regard to the issues surrounding the treatment of discolored lead white on paper artifacts.

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NOTES

1. A survey of practicing paper conservators was carried out by the author in 2003. Participants responded to a six-question written questionnaire that addressed current and past treatment methodology and related observations.
2. Also presented at the 2006 AIC meeting, in celebration of the twenty-fifth anniversary of the Book and Paper Group, but not included here, was a survey of historical and contemporary treatment methods as reflected in the literature and in conservation practice.
3. Not explored in this study is the use of ethanol or other alcohols to facilitate conversion treatment. Conservators use alcohols in a variety of ways, from adding a drop or two to an aqueous peroxide solution, to pre-wetting much like one does to facilitate penetration of a consolidant, or via brush application of a 1:1 hydrogen peroxide:ethanol mixture. The distinct differences in treatment approach suggest that a separate investigation evaluating the impact of treatment methods employing alcohol would be beneficial.
4. The hydrogen peroxide was introduced via a peroxide-impregnated blotter through Gore-Tex.

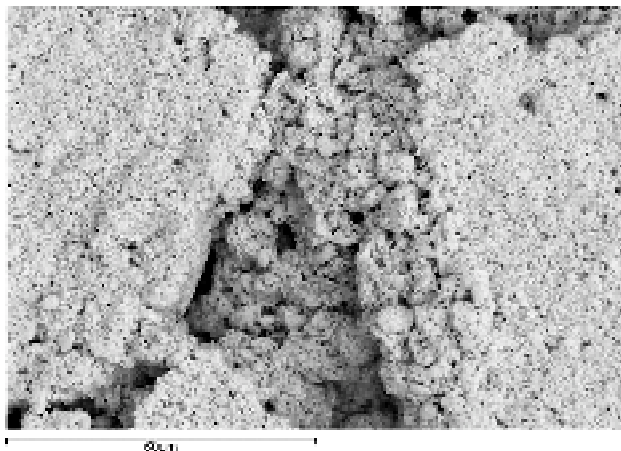


Fig. 6. Treated sample. Brush, 1:1 30% hydrogen peroxide and ether. 1000x magnification (SEM). Ruptured area of paint film.

5. For an in-depth discussion and detailed description of gel preparation see Margo McFarland's article listed in the references.

6. Referred to as the "standard method" in the article by Daniels and Thickett listed in the references. After mixing, the solution separates into two distinct layers, the top being a peroxide-ether mixture of low peroxide concentration that becomes the working solution.

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