The Whitening Effects of Peroxide Gels on Darkened Lead White Paint¹

INTRODUCTION

Hydrogen peroxide -- in both aqueous and organic solvent solutions -- has long been used by conservators to convert darkened lead white [lead sulfide (PbS)] to lead sulfate [PbSO4], which is white and has morphological characteristics nearly identical to those of the original artist's material, basic lead carbonate [Pb(OH)2 2PbCO3]. As many conservators know from experience, peroxide conversion treatments are not always successful, especially in cases where lead white paint, bound with a water soluble agglutinant, has blackened over centuries and where the crystalline structure of the lead sulfide complex is particularly stable. Disturbing from an aesthetic stand-



point is the situation where a peroxide treatment results in the partial conversion of lead sulfide to lead sulfate, with a concomitant partial color reversion from black to gray.²

This paper is organized into four sections. The first discusses the treatment project that initiated the use of peroxide gels and the thinking that went into the development of the technique; the second offers an explanation of how the addition of cellulose ether to peroxide solutions achieves successful results; the third provides a basic recipe for the gel mixture and a description of a standard technique used for its application; and the fourth addresses the issue of what affect cellulose ether residues may have on works of art treated using this technique.

BACKGROUND

Between 1987 and 1997 over seven hundred drawings in the collection of the Department of Prints and Drawings at The Art Institute of Chicago were systematically examined in preparation for the catalogue Italian Drawings before 1600 in The Art Institute of Chicago (fig. 1).³ Through the course of this project it became clear that a significant number of these works suffered from lead white oxidation. The drawings were tested to assess the sensitivity of the discolored paints to combinations of hydrogen peroxide (up to a concentration of 5%) and ethyl alcohol.⁴ Those that proved to be responsive were then treated.⁵ The majority of the drawings, however, were unresponsive to the oxidizing agent. As a result, important works which were often in superb condition, aside from their disfigurement, were considered unexhibitable; others were disfigured to the extent of illegiblity and were thus of little use to the arthistorical community.

A particularly patent example, A Design for a Façade Decoration by an artist in the circle of Girolamo Gegna (circa 1548), was the subject of numerous testing campaigns (fig. 2a). This drawing remained in a drawer of the conservation lab for years, and was often the subject of discussion with visiting colleagues. The composition was executed in







brown ink, and lead white on a dark, blue-green primary support. The pen and ink lines and thin ink washes were applied with a delicate hand, so that contrast between the sheet and drawn line is not strong. Sulfuration of much of the lead white paint was so complete that the degraded areas were black and even reflective. The lead sulfide imparted high contrast to the image, and was the visual element by which much of the composition was unintentionally articulated (fig. 2b). The greatest fear in treating this piece lay in the potential for a partial conversion of the lead sulfide to lead sulfate, which would render the drawing uniformly middle-toned, decreasing the legibility of the composition.

Before returning A Design for a Façade Decoration to the vault (thereby giving up on prospects for reversion) a morning in early April of 1996 was dedicated to further testing with alkalized peroxide/solvent combinations (ethyl alcohol and acetone). Hydrogen peroxide, in a concentration as high as 5%, was tested but proved ineffective. In order to increase the exposure time between the darkened lead white and the oxidizing agent, methyl cellulose was mixed with a solution



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of equal parts 3% aqueous hydrogen peroxide (pH 7.5) and ethyl alcohol and brushed onto a line of discolored white heightening. The peroxide gel took less than three seconds to revert all of the test area from black to white. Other areas were tested and successfully reverted as well (fig. 2c). The entire treatment of *A Design for a Facade Decoration* required less than two days to complete (fig. 2d). One of the benefits of the new technique was soon revealed. The gel did not penetrate the paper. Acting as a poultice, the cellulose ether prevented inadvertent saturation of the primary support.

With the success of this first treatment, dozens of lead sulfide-disfigured drawings were brought by curators Laura Giles and Suzanne McCullagh, co-authors of the catalogue, to the paper conservation lab. Over fifty recalcitrant pieces were tested, and the vast majority reverted completely using the peroxide gel technique.⁶ As a result, many drawings that were formerly considered "lost causes" figure prominently in the catalogue (figs. 3a-5b), and more than a dozen were included in the exhibitions "Highlights of Italian Drawings" and "Drawings Rediscovered," recently on view at The Art







Fig. 2c.



Fig. 3a. Before treatment

Institute of Chicago. The cellulose ether/peroxide poultices worked remarkably well to convert the lead sulfide to lead sulfate, but the question was, why? To investigate, the most comprehensive body of information related to peroxide gel chemistry was consulted - that found within the library of the American Dental Association, whose national headquarters is conveniently located ten blocks north of The Art Institute.



Fig. 3b. After treatment

FACTORS THAT AFFECT HYDROGEN PEROXIDE-INDUCED OXIDATION

Dental bleaching literature provides a concise description of the six major factors that affect hydrogen peroxide-induced oxidation in stained teeth. A succinct chart in *Complete Dental Bleaching*,⁷ can serve as a guide for considering how the same factors affect hydrogen peroxide induced oxidation of lead sulfide on paper (fig. 6). They



Fig. 4a. Before treatment



Fig. 4b. During treatment



Fig. 4c. After treatment

are assessed for their applicability to works of art on paper as follows:

Factor 1: Surface Debridement

The purpose of this dental procedure, which might seem to be analogous to surface cleaning in the conservator's approach to treatment, is not to make teeth whiter and brighter, but instead to prepare the surface of the dentin for the penetration of the peroxide solution. In fact, for difficult stains, the dental literature recommends lightly etching the dentin to maximize penetration.

The issue of peroxide penetration within the context of lead sulfide conversion is central to the efficacy of such treatments. Through experience it has been determined that in particularly severe cases, where the lead sulfide is very dark and very dense, the surface of the metallic salt resists penetration (figs. 7a-d). In these cases aqueous peroxide solutions (with or without the addition of cellulose ethers) will have minimal or no effect. However, when the same discolored paints are brushed with ethyl alcohol immediately before the application of the peroxide gel, the reaction usually proceeds, suggesting that alcohol saturates the lead sulfide, permitting penetration of the subsequently applied oxidizing agent (fig. 7d).⁸

The addition of ethyl alcohol to the peroxygenated cellulose ether solution also promotes the saturation of the oxidizing agent into degraded paint. However, the presence of ethyl alcohol in the system sometimes counteracts the poulticing effect of the gel, causing penetration of the oxidizer into the primary support. The issue of penetration of the peroxide solution into the underlying primary support will be taken up in greater detail below.

Factor 2: Hydrogen Peroxide Concentration

In their paper "The Reversion of Blackened Lead White on Paper,"9 Vincent Daniels and David Thickett state that lead sulfide, the product of lead ions in solution and hydrogen sulfide, is readily converted to lead sulfate in the presence of minute amounts of hydrogen peroxide, quantitatively given as 1 part in 1,250,000.¹⁰ Therefore, in theory, the oxidation reaction should proceed in extremely dilute solutions of hydrogen peroxide. The fact that it often does not, even in aqueous and ethyl alcohol solutions of concentations higher than 3%, requires further research. It seems clear that the slower the sulfuration of lead carbonate and the longer lead sulfide is present, the more stable the crystalline degradation product will become over time. This, however, does not explain why some darkened lead white paints revert while others do not, even with the use of peroxide gels.¹¹

A case in point is the mid-16th-century Florentine drawing *Holy Family in Joseph's Carpentry Shop*, by a follower of Jacopa da Empoli (fig. 8a). Before treatment the drawing exhibited a range of discoloration -- black,



Fig. 5a.

brown, orange, and gray. A test with a gel solution to the right arm of the industrious Child resulted in the total conversion of the lead sulfide, and thus the treatment was carried out. After-treatment documentation demonstrates that the effort was successful only with respect to certain passages of discolored paint (fig. 8b). The fine, thin, delicately applied lines of white heightening used to articulate and emphasize the forms of Mary and the Child readily reverted, while the more arbitrarily applied lines did not. Microscopic investigation after treatment revealed that in numerous places the unresponsive paint was applied on top of the finer, more precise lines of converted lead white, demonstrating that additions had been made by a later hand. The original heightening (the older paint) proved to be dramatically more responsive than the retouching, and treatment made the later additions readily apparent.

Factor 3: Temperature

Although exposure to excessive heat is detrimental to works of art on paper, some warmth -- such as that impart-



Fig. 5b.

ed by a task lamp or light table -- will undoubtedly encourage the conversion reaction. $^{12}\,$

Factor 4: pH

Hydrogen peroxide is an oxidizing agent that has the ability to produce free radicals, HO_2 and O \cdot .¹³ When hydrogen peroxide in pure aqueous form is stored and shipped, an acidic pH must be maintained to extend its shelf life.¹⁴ At an acidic pH a larger percentage of the weaker free-radical, O \cdot , is produced. The perhydroxyl, HO2 \cdot , is the more potent free radical and its production is boosted in an alkaline environment, ideally to a pH level of 9.5 to 10.8. Of course this degree of alkalinity exceeds the safety threshold for cellulose and media; but clearly, conservators should use elevated pH to maximize the efficacy of peroxide-induced oxidation.

Factors 5: Time

The initial rationale for using hydrogen peroxide in the form of a poultice was based on the assumption that the success of the lead sulfide conversion treatment relates directly to the duration of exposure.

- 1. Surface debridement: Thorough scaling and polishing should be performed in order to eliminate all superficial debris.
- 2. Hydrogen peroxide concentration: The higher the concentration, the greater the effect of the oxidation process. The highest concentration generally used is 35% hydrogen peroxide.³ Note: When gelling agents are added to a 35% solution of hydroden peroxide, the concentration of H_2O_2 is then reduced to 25%.
- 3. *Temperature:* An increase of 10 °C doubles the rate of the chemical reaction. Generally, if the temperature is elevated to a point at which the patient does not feel discomfort, then the procedure is taking place at a safe range of temperature.¹²⁻¹⁵
- 4. pH: When hydrogen peroxide is stored and shipped, an acidic pH must be maintained to extend shelf life. The optimum pH for hydrogen peroxide to have its oxidation effect is pH 9.5 to pH 10.8. This produces a 50% greater result in the same amount of time as at a lower pH.^{2,3}
- 5. *Time*: The effect of the bleach is directly related to the time of exposure. The longer the exposure, the greater the color change.¹⁵
- 6. Sealed environment: Placing the hydrogen peroxide into a sealed environment has been shown to increase its bleaching efficiency.¹

Factor 6: Sealed environment

Carbamide peroxide (also known as hydrogen peroxide carbamide, carbamide urea, or perhydrol urea), a material found in most dental bleaching agents, is used by dentists because it breaks down directly into hydrogen peroxide. (A 10% carbamide peroxide solution will produce a 3% hydrogen peroxide equivalent.)

An important additive to carbamide peroxide is the synthetic polymer thickening agent Carbopol (B.F. Goodrich). Carbopol renders the hydrogen peroxide thixotropic, and thus retentive to the dentin substrate. Carbopol also slows the rate of oxygen release, extending the duration of the bleaching action (see factor 5). Frequent reference is made in dental literature to the significant fact that a 10% solution of carbamide peroxide (which, again, produces a 3% hydrogen peroxide equivalent) -- in combination with the Carbopol gel -- permits safe and effective dental bleaching where 30% - 35% hydrogen peroxide solutions might otherwise be used.¹⁵ The effect of cellulose ethers in hydrogen peroxide formulations for the conversion of lead sulfide to lead sulfate would appear to be analogous to that of the bleaching formulations commonly used by dentists. In their paper referenced above, Daniels and Thickett state that "loss of hydrogen peroxide can be caused by evaporation, reaction, or decomposition."¹⁶ In the presence of a cellulose ether, evaporation and decomposition of hydrogen peroxide are controlled. The oxidizing material itself is locked up in a relatively non-aerobic ("sealed") environment, reducing the likelihood that the unstable perhydroxyl radical will react with air. By eliminating this competing reaction, the perhydroxyl radical is more likely to react with the lead sulfide complex, producing white lead sulfate.

Empirical results of using gels to control some of the factors that affect the conversion of lead sulfide to lead sulfate suggest that the efficiency of peroxide is boosted in the presence of such gels. In other words, percentages for dilution of hydrogen peroxide can be significantly reduced from the percentages that traditionally have been employed



Fig. 7a.



Fig. 7c



Fig. 7b.



Fig. 7d

to achieve the same results. Furthermore, because hydration can be maintained with gels, repeated application of the oxidizing agent is generally not necessary. The direct implication of this feature is that the concentration of peroxide is more easily regulated. As Daniels and Thickett have demonstrated through their analysis of peroxide content in paper, applications of hydrogen peroxide are additive, for "hydrogen peroxide is deposited in the paper each time a fresh application of ... peroxide is made. Each application increases the peroxide content of the paper".¹⁷



Fig. 8a.

Because gels are thixotropic and permit poulticing, it is very often possible to adjust gel formulation in such a way as to prevent saturation of the paper underlying the darkened lead white. Thicker solutions of peroxide gels can be used to retard hydrogen peroxide saturation for absorbent papers, while very thin solutions can be employed in cases where the primary support is well sized.

GENERAL GUIDELINES FOR THE FORMULATION AND USE OF THE GEL

1. Start with a 3% acetic acid-stabilized aqueous solution of hydrogen peroxide, alkalized to an appropriate pH. Although pH levels were generally limited to 8.5 through the course of this project, a .5 increase in pH to 9 dramatically boosted the rate of reaction for particularly stubborn cases. For readily reactive lead sulfide, the peroxide concentration should be reduced (through the addition of alkalized water) to the lowest level wherein successful results are still achieved.

2. To the alkalized hydrogen peroxide add a viscous solution of the appropriate cellulose ether, remembering that the addition of the gelling agent will reduce the concentration of the hydrogen peroxide. Stir gently (to reduce the formation of air bubbles) or cover and allow





to sit in a refrigerated environment until viscosity becomes uniform. (Warm to at least room temperature before application.) The viscosity of the gel should be determined on the basis of the absorbency of the support, and -- in some instances -- on the friability of the darkened paint. High viscosity will usually counteract the wetting effect of organic solvent admixtures. When treating non-absorbent papers it is advisable to use extremely dilute concentrations of cellulose ether. The slightest presence of the gelling agent is sometimes all that is required to create the sealed environment phenomenon. The peroxide gels used to convert the discolored lead white on the 16th-century Italian drawings was generally of very low viscosity -- just noticeably more viscous than the aqueous peroxide itself.

Using the gel:

1. For particularly dense, crystalline, recalcitrant examples of darkened lead white, wet the paint with ethyl alcohol. If the primary support is inadvertently wetted, allow the ethyl alcohol to evaporate from the paper before applying the peroxide gel solution.

2. Apply the peroxide gel to the surface of the paint using a fine, soft brush. The gel should be at room temperature or slightly warmer.

3. Allow the peroxygenated gel to sit on the surface of the paint, making sure that it does not evaporate. To prevent evaporation, simply re-hydrate with alkalized, deionized water (or a very dilute solution of aqueous hydrogen peroxide) by simply touching the wetted tip of the brush to the surface of the gel. Mechanical distress to the paint is thus avoided during the process of the chemical conversion. Between three seconds and ten minutes will generally be required for the reaction to proceed to completion.

4. Clear the solution by wicking it through desiccated cellulose (very thin blotters or fine swabs), followed by rehydration of the gel, wicking again, and repeating this process until the gel is cleared to satisfaction.

CELLULOSE ETHER RESIDUES

A microscopic layer of cellulose ether residue will remain when this technique is employed, just as it will when cellulose ether is used as a poultice for adhesives, as a sizing agent, as a surfactant, etc. This fact might seem disturbing at first, but upon closer consideration, the benefits of cellulose ether residues become apparent. The conservation literature that discusses the conversion of lead sulfide to lead sulfate rarely addresses the fact that all of the metallic salts in question -- lead carbonate, lead sulfide, and lead sulfate -- have different physical properties. It has been observed through the course of treatment that in converting lead sulfide to lead sulfate, the paint layer undergoes physical changes, becoming more porous and more brittle.¹⁸ In using the peroxide gel technique, the cellulose ether "residues" can serve to consolidate the potentially more unstable reaction product, lead sulfate.

Another benefit of the cellulose ether residue relates to the fact that it imparts a protective skin on the surface of the lead sulfate, thereby isolating it from recurrent exposure to sulfurous gases. Lead sulfate is not inert. It, like basic lead carbonate, reacts with sulfurous gases to form lead sulfide. This fact was well known during the industrial revolution, a time when sulfurous gases were omnipresent. The nineteenth-century text, *A Descriptive Handbook of Modern Watercolor Pigments*, published in 1887, asserts that blackened lead white in old watercolor drawings "sometimes ... may be satisfactorily restored by applying a solution of peroxide of hydrogen ; but the





whiteness (due to the oxidation of black sulfide of lead into white sulphate of lead) is only temporary, and it has been stated to be even more liable to discoloration than before".¹⁹

A contemporary occurrence of lead white discoloration dramatically substantiates this observation. The drawing The Virgin and Child with Saints John the Evangelist, Anne (?), Joseph, and a Female Saint by Giulio Clovio (fig. 9), was part of the recent exhibition, "Michelangelo and His Influence: Drawings from Windsor Castle," which traveled to five venues. It was executed in gray chalk and gold paint on laid paper. A small patch of lead white gouache is located on the right hip of the Child. The paint is thought to have been used to obscure an imperfectly drawn passage of the Child's torso, or possibly to cover a defect in the primary support.²⁰ In 1995, before being reproduced for the exhibition catalogue of the same title, the drawing was examined and lead white oxidation was observed. The discolored paint was treated with ethereal peroxide, and reverted to white.²¹ By mid-1996, the paint had become black again. A second peroxide treatment reconverted the lead sulfide to lead sulfate and the drawing was framed for exhibition. After exhibition at the second venue, a "noticeable grey creeping around the edges of the patch²² was noted. Three days later, after travel to the third venue, The Art Institute of Chicago, the patch was "thoroughly greyblack, although it had been transported in sealed cases amongst other drawings with a sheet of Artsorb.²³ On the basis of the characteristics of the Clovio drawing, the nature of the media, and the reactive nature of lead sulfate, the gel technique for peroxide-induced reversion presents an attractive treatment option, and one that will likely be explored in the near future. Further research will determine the extent to which the protective properties of peroxide gels will inhibit recurrent oxidation.

CONCLUSION

Hydrogen peroxide gels present numerous benefits in the treatment of darkened lead white paints. To state as much, is not to suggest that this approach is superior to any other. Ethereal peroxide treatments are often appropriate and effective, but not always a desirable approach. Hydrogen peroxide vapor treatments can also be appropriate and effective for some types of works of art. The treatment campaign that inspired the development of this novel technique took into account one critical factor -- had peroxide gels not been used, no conversion would have taken place. The project described above presented numerous treatment challenges that the peroxide gel technique successfully and gratifyingly addressed.

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NOTES

1. This article is concerned with lead white in combination with water-soluble binders only.

2. The terms "reversion" and "conversion" are frequently misused in the conservation literature. For clarification, reversion refers to the change in color from black to white, whereas conversion refers to the chemical reaction of lead sulfide to lead sulfate. Sulfur-induced lead white discoloration can also take on pink, orange, and brown coloration. It has been observed that these types of discoloration often precede the formation of black lead sulfide, but their chemical composition is not known. For further information see: Claire L. Hoevel, "A Study of the Discoloration Products Found in White Lead Paint Films," in Jeffrey Abt, editor, *The Book and Paper Group Annual 4* (1985) (Washington: The American Institute for Conservation, 1986), pp. 35-42."

3. Suzanne Folds McCullagh and Laura Giles, *Italian Drawings* before 1600 in The Art Institute of Chcago, (Chicago: The Art Institute of Chicago, 1997).

4. Although ethereal peroxide has long been employed by conservators to effect the oxidation of lead sulfide, its use was not an option. Chemicals as unstable as diethyl ether are not kept or used in any of the six conservation laboratories at The Art Institute.

5. Both liquid and vapor phase treatments were carried out. Some of these treatments proved to be only partially successful. Subsequent treatment with peroxide gels caused the lead sulfide in these drawings to convert completely.

6. Ethyl hydroxyethyl cellulose and carboxymethyl cellulose were also effectively employed as gelling agents. The use of sodium hydroxymethyl cellulose was avoided however, due to the fact that it can form insoluble complexes in the presence of metal ions. For more on cellulose ethers see: "Adhesives," *Paper Conservation Catalogue*, (Washington: Book and Paper Group of the American Institute for Conservation, 1994), 9th Edition, pp. 21-33.

7. Ronald E. Goldstein and David A. Garber, *Complete Dental Bleaching*, (Chicago: Quintessence, 1995), p. 32.

8. The benefit of using ethyl alcohol to induce the conversion reaction was evidenced while demonstrating the peroxide gel technique to the paper conservation staff at The Metropolitan Museum of Art in July of 1997. In testing the technique on a small, lead sulfide-disfigured portrait (executed in black chalk and lead white), a small drop of a viscous peroxide gel solution was placed on the surface of a field of very blackened lead white paint. The test area, which had not been pre-wet with ethyl alcohol, resisted reaction. After four minutes, with very little chemical change having taken place, ethyl alcohol was touched to the surface of the gel. The paint at the circumference of the hemi-spherical daub of gel (i.e. the point of contact between the ethyl alcohol, the gel, and the lead sulfide) became wetted and a circle of white lead sulfate became apparent within seconds.

9. Vincent Daniels and David Thickett, "The Reversion of Blackened Lead White on Paper," in Sheila Fairbrass, editor, *The Conference Papers Manchester 1992* (London: The Institute of Paper Conservation, 1992), pp. 109-113.

10. Ibid., p. 109.

11. Note that gelling agents reduce the concentration of hydrogen peroxide.

12. In testing the effectiveness of peroxide gels on discolored lead white paint, one colleague imparted warmth by carrying out the treatment on top of a piece of thick Plexiglas, under which a rheostat-adjusted heating pad had been placed. The consequence of even slightly elevated heat was said to be marked.

13. Goldstein and Garber, Complete Dental Bleaching, p. 34.

14. This brings up the question of how commercially available hydrogen peroxide solutions are stabilized. In conversation with technical representatives from Fisher Scientific and Baxter Scientific Products it was learned that all solutions of hydrogen peroxide sold by these companies are stabilized, regardless of the dilution or grade of the product. All 30% solutions are stabilized with sodium stannate. Some 3% solutions are stabilized with sodium stannate while others are stabilized with glacial acetic acid. Unfortunately, because scientific catalogues do not always identify stabilizers, a phone call to the supplier is required to determine this information.

15. For more see: James Mellard, "Effects of a Carbamide Peroxide Bleaching System," (thesis paper, University of Texas at Houston, 1992). See also: Gerald McLaughlin and George Freedman, *Color Atlas of Tooth Whitening*, (St. Louis: Ishiyku EuroAmerica, 1991).

16. Daniels and Thickett, p. 112.

17. Ibid., p. 111.

18. In A Textbook of Mineralogy the mineral form of lead sulfate, anglesite, is characterized as "very brittle" whereas the mineral form of lead sulfide, galena, bears no such characterization. Edward S. Dana, A Textbook of Mineralogy, revised and enlarged by William E. Ford, 3 volumes, 4th edition, (New York: John Wiley & Sons, 1932), pp. 416 & 752.

19. A Descriptive Handbook of Modern Water Colour Pigments, (London: Winsor & Newton, c. 1887), p. 35.

20. Personal communication with Martin Clayton, Assistant Curator, The Royal Collection, Windsor Castle, April 10, 1997.

21. Paul Joannides, Michelangelo and His Influence: Drawings from Windsor Castle, (London: Lund Humphries, 1996). The illustration of The Virgin with Child and Saints appears on p. 91.

22. Personal communication with Martin Clayton, Assistant Curator, The Royal Collection, Windsor Castle, April 10, 1997.

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