The Influence of Pigments and Ion Migration on the Durability of Drying Oil and Alkyd Paints

Marion F. Mecklenburg, Charles S. Tumosa, and Edward P. Vicenzi

ABSTRACT. The durability of paints made with drying oil and alkyd mediums refers to their resistance to atmospheric moisture and solvents used in the cleaning of paintings. Ideally, after a reasonable drying period, these paints develop sufficient polymerization and cross-linking to resist swelling and deterioration from most cleaning solvents. Although there has been considerable research on the effects of certain metal ions on the autoxidation of drying oils, that research cannot be used to determine the long-term stability of paints made with drying oils. Current research suggests that a wide variety of metal ions affects the ultimate film formation of oil paints. The exact reaction of those ions with the drying oils is not clearly understood. But there is now considerable evidence that those metal ions are not only capable of migrating throughout a given paint layer but also sufficiently mobile to migrate from one paint layer to an adjacent one in a painting. In this case the migrating ions are capable of either enhancing or degrading the adjacent paint layers. Because artists' alkyd paints contain considerable levels of drying oils, they can react with pigments in an manner analogous to oil paints and therefore will be part of this discussion.

INTRODUCTION

To a practicing painting conservator it can be puzzling that oil paints made with specific pigments, such as organic reds and blacks and some of the earth colors, are easily and safely cleaned on some paintings whereas they are quite sensitive to solvents on others. The question regarding the resistance to damage from cleaning solvents comes down to what enhanced the durability of these paints.

There has been considerable research on the effects of certain metal ions on the autoxidation of drying oils. For example, it has been shown that metal ions such as Co^{2+}, Mn^{2+}, and Fe^{2+} are considered "primary" driers and act during oxidation, whereas Pb^{2+}, Zr^{4+}, and Al^{3+} are "secondary" driers and are active during polymerization. Finally, Ca^{2+}, K^{+}, and Zn^{2+} are considered auxiliary driers as they act to modify the activity of the primary driers (van den Berg, 2002; Tumosa and Mecklenburg, 2005). More importantly, it is generally agreed that the ability of a metal compound to catalyze the oxidation of the oil and form a film depends upon both the solubility and the dissociation of the metal ion in the oil (Olson, 1921; Marling, 1927; Bennett, 1941; Morgan, 1951; Stewart, 1967). In order to get sufficient concentrations of metal ions to catalyze the oxidation of the oil, either the metal ions must be added separately (dissolved or reacted) or the metal ions must dissolve from the pigment itself. Dissociation into metal ions is quite important, and a compound such as tetraethyl lead, which has covalent bonding and does not dissociate, exerts no influence on the drying of oil (Bennett, 1941). The requirement for a metal ion

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to catalyze the oxidation of the oil is accurate, since unpigmented linseed oil will not form a durable film.

Historically, research on the effects of pigments on paint film formation has been considerably less extensive, with reason. It simply takes a long time to see the actual effects of the pigments on the durability of the paint made with them (van den Berg, 2002). Over the past 30 years, a systematic study of the effects of pigment on the natural drying of oil paints has been conducted. For the past 20 years the paint study at the Museum Conservation Institute of the Smithsonian Institution has included "control paints" specifically manufactured with known pigments, oils, and driers. Some paints are still undergoing modification after 20 years. Some of the results are of interest to those concerned with the preservation of objects containing oil paints.

THE INFLUENCE OF PIGMENTS ON THE MECHANICAL PROPERTIES OF OIL PAINTS

Oil paints made with basic lead carbonate form a remarkably tough and durable film. This paint will continue to change its mechanical properties over a long time, as shown in Figure 1. This figure shows that the white lead paint continues to get stiffer and stronger even after more than 18 years of drying. This is an indication that the paint is still chemically active. This same paint is also fairly resistant to the solvents, as shown in Figure 2, where little change in the mechanical properties of the paint is observed when exposed to water and four different solvents and allowed to dry for 30 days or more.

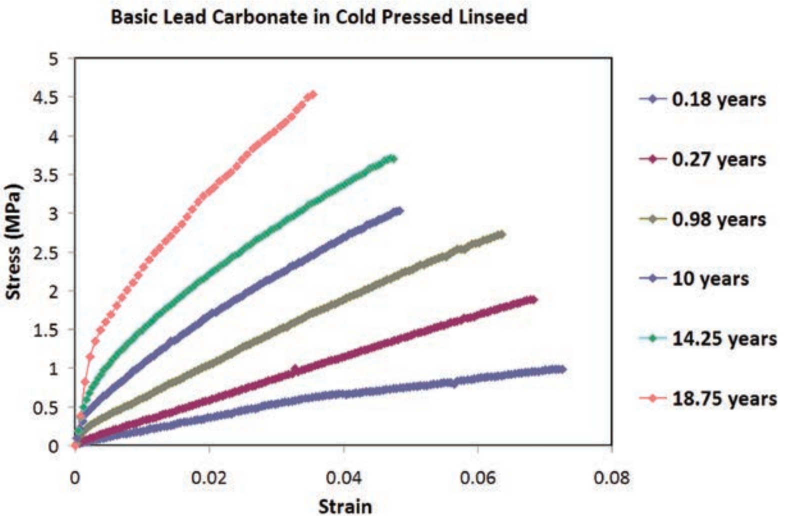

FIGURE 1. Mechanical properties of basic lead carbonate ground in cold-pressed linseed oil. This paint continues to get stiffer and stronger after 18.75 years of drying.

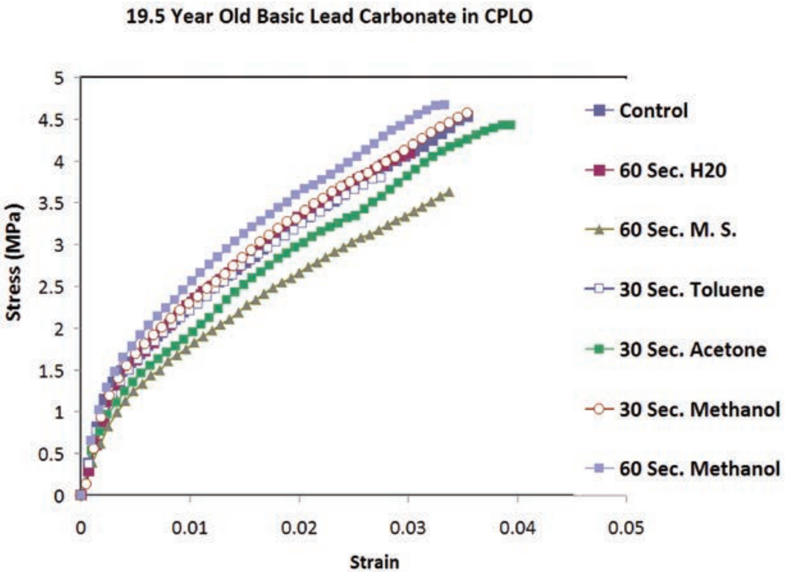

FIGURE 2. Mechanical properties of basic lead carbonate ground in cold-pressed linseed oil (CPLO) before and after being exposed to water and to four different solvents. Any stress-strain plot lower than the control plot is indicative of solvent retention, and this tends to increase the paint's flexibility. This is illustrated by the exposure to mineral spirits (M.S.).

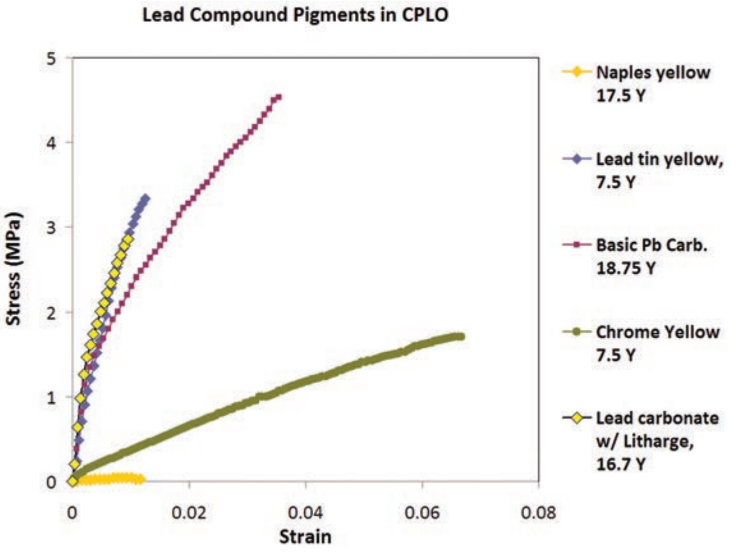

FIGURE 3. Mechanical properties of paints made with cold-pressed linseed oil and five different lead compound pigments. The Naples yellow does not form a durable film even after 17.5 years of drying.

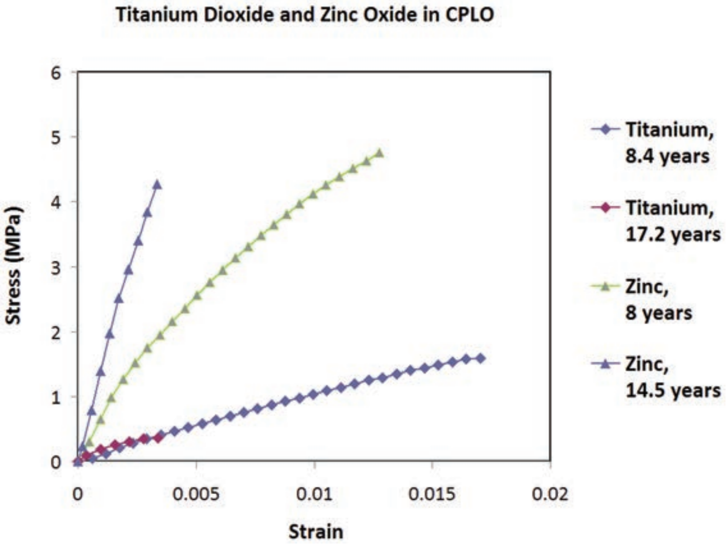

FIGURE 4. Mechanical properties of paints made with cold-pressed linseed oil and zinc oxide and titanium dioxide (rutile). The paint made with the zinc oxide becomes quite brittle, and the paint made with the titanium oxides becomes weak.

However, not all lead compounds form durable paint films. Figure 3 shows the mechanical properties of paints made with cold-pressed linseed oil and five different lead compound pigments. The paints made with lead tin yellow and basic lead carbonate with 1.6% lead monoxide become extremely brittle. The lead compound $Pb(SbO_3)_2Pb_3(Sb_3O_4)_2$, known as Naples yellow, shows very poor film formation. Even after 17.5 years of drying, this paint will completely dissolve in either acetone or methanol after 30 s.

Oil paints made with zinc oxide and cold-pressed linseed oil will become extremely brittle in about three years. They are ultimately capable of delaminating adjacent paint layers made with that pigment and even with other pigments. Paints made with titanium dioxide (rutile) will dry to a very weak paint film. Figure 4 shows the mechanical properties of paints made with titanium dioxide and zinc oxide ground in cold-pressed linseed oil.

Perhaps of greater importance are paints made with the earth colors such as umber, ocher, and Sienna, organic pigments such as alizarin madder, and even cobalt. These will hydrolyze in a very short time, causing the paints to become vulnerable to atmospheric moisture and cleaning solvents (Tumosa and Mecklenburg, 2005). Figure 5 shows the mechanical properties of paints made with cold-pressed linseed oil and the pigments raw and burnt Sienna and raw and burnt umber. Paints made with these pigments appear to develop durable films initially, but as they begin to hydrolyze early in their drying history, they experience a serious loss of mechanical properties such as strength and stiffness as time goes on.

If one of the paints that hydrolyzed is exposed to solvents, the film is seriously altered. Figure 6 shows an 18-year-old raw umber in cold-pressed linseed after drying from a 30 s exposure to acetone. The paint shows distinct cracking in addition to what other changes that may take place.

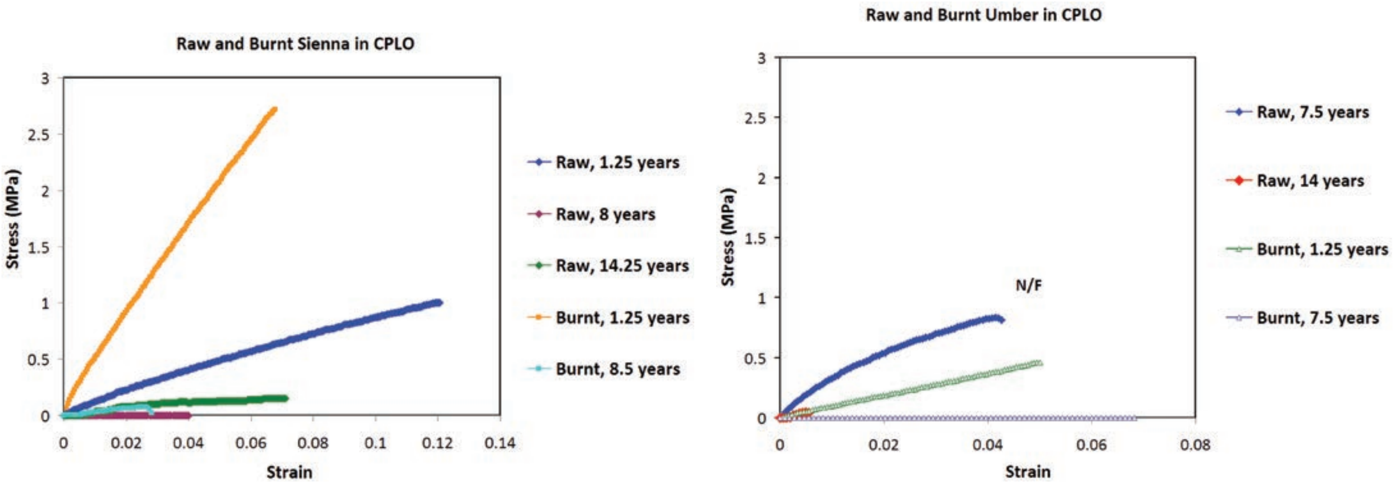

FIGURE 5. Mechanical properties of paints made with cold-pressed linseed oil and the pigments (left) raw and burnt Sienna and (right) raw and burnt umber. The paints made with these pigments appear to develop durable films initially but begin to hydrolyze early in their drying history. N/F indicates that the test was terminated before the sample actually broke.

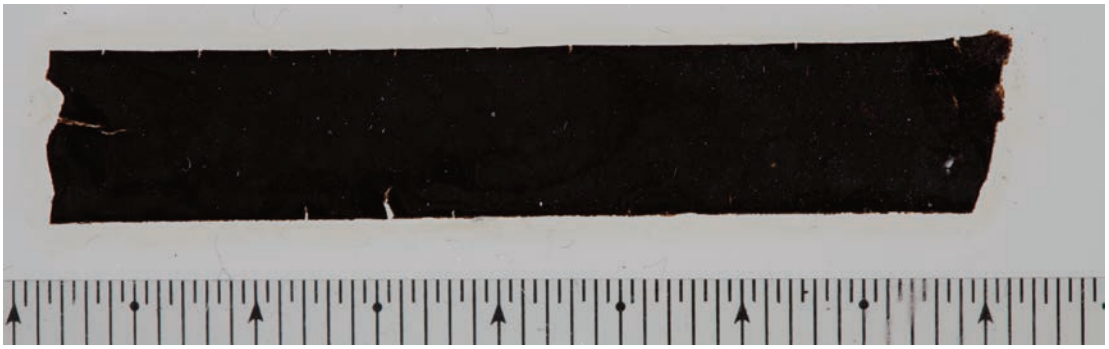

FIGURE 6. An 18-year-old raw umber in cold-pressed linseed after drying from a 30 s exposure to acetone. The cracking will cause loss of stiffness and strength in the paint.

Continued testing of both the mechanical properties of paints and their exposure to solvents leads to the conclusion that resistance to solvents correlates with better mechanical properties. The stiffer and stronger a paint is, the more resistant to solvents it becomes. This is because of the enhanced cross-linking and polymerization. Other paints that show loss of properties after initially appearing to dry normally are yellow ochre, red iron oxide, alizarin madder lake, lamp black, Van Dyke brown, and cadmium yellow.

THE INFLUENCE OF PIGMENTS ON ALKYD PAINTS

It was shown in Figure 4 that zinc oxide will cause an oil paint to become extremely brittle and it was shown that the addition of manganese to burnt umber oil paint can also cause it to turn brittle (Tumosa and Mecklenburgh, this volume). Figure 7 shows the mechanical properties of 7-year-old alkyd paints made with titanium dioxide, cobalt blue, and zinc oxide. The paint made with the zinc has become quite brittle.

Figure 8 shows the mechanical properties of 29-year-old alkyd paints made with titanium dioxide, lead carbonate, titanium dioxide containing zinc oxide, burnt umber containing manganese, yellow ocher, ivory black, and alizarin crimson. The paints containing the zinc oxide, manganese, and lead carbonate become quite brittle, whereas those containing yellow ocher, ivory black, and alizarin crimson remain flexible.

Over time the alkyd paints become more and more resistant to solvents. Figure 9 shows the exposure to solvent has little effect on the mechanical properties of the 29-year-old alkyd paint made with alizarin crimson. It also shows the mechanical

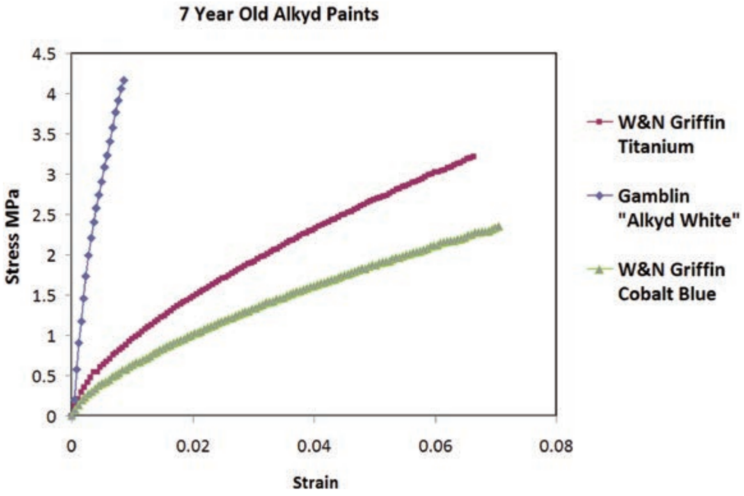

FIGURE 7. Mechanical properties of 7-year-old alkyd paints made with titanium dioxide, cobalt blue, and zinc oxide. The paint with the zinc oxide pigment becomes quite brittle.

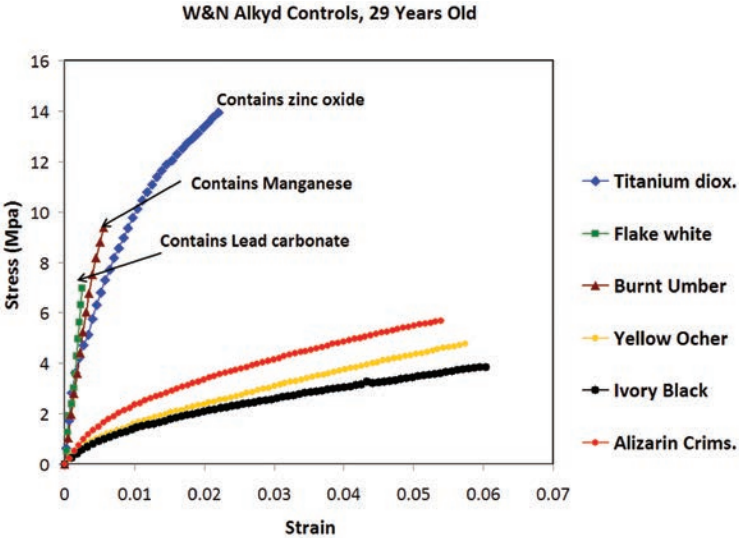

FIGURE 8. Mechanical properties of 29-year-old alkyd paints made with titanium dioxide, lead carbonate, titanium dioxide containing zinc oxide, burnt umber containing manganese, yellow ocher, ivory black, and alizarin crimson. The paints containing the zinc oxide, manganese and lead carbonate become quite brittle.

properties of the alkyd paint when tested after 20 and 29 years of drying and shows that they were still changing. In general, all of the 29-year-old alkyd paints tested and made with yellow ocher, titanium, burnt umber, lead carbonate, alizarin crimson, and ivory black showed considerable resistance to exposure to methanol and acetone.

THE EFFECTS OF MIXING PAINTS ON THEIR MECHANICAL PROPERTIES AND DURABILITY

If an oil paint made with an earth color or an organic pigment is mixed with a lead white paint, the lead contributes to the film-forming process of the mixture, and a durable film can result. This can happen even though the lead paint content comprises less than 25% of the mixture, and it is possible that the concentration of the lead paint could be much smaller and still be effective. Inadvertent or intentional mixing of even small amounts of paint on an artist's pallet might have an effect. In June 2007, three paints, yellow ocher, terre verte, and alizarin madder lake, all ground in cold-pressed linseed oil, were mixed with Grumbacher flake white in alkali-refined linseed oil. The pigments in the flake white are lead carbonate and zinc oxide. The mixtures of the paints were one part white to four parts of the colored paints by volume. The paints were tested after 2.5 years of drying. Figure 10 (left) shows the mechanical properties of the 2.5-year-old mixed yellow ocher paint and pure yellow ocher paints that had dried much longer. The 18-year-old yellow ocher in cold-pressed linseed and the 29-year-old commercial (Speedball) yellow ocher paints hydrolyzed and retained no strength. The 30-year-old commercial (Winsor and Newton) yellow ocher developed some strength, but it is possible that some drier was added to this paint, although none was detected during analysis.

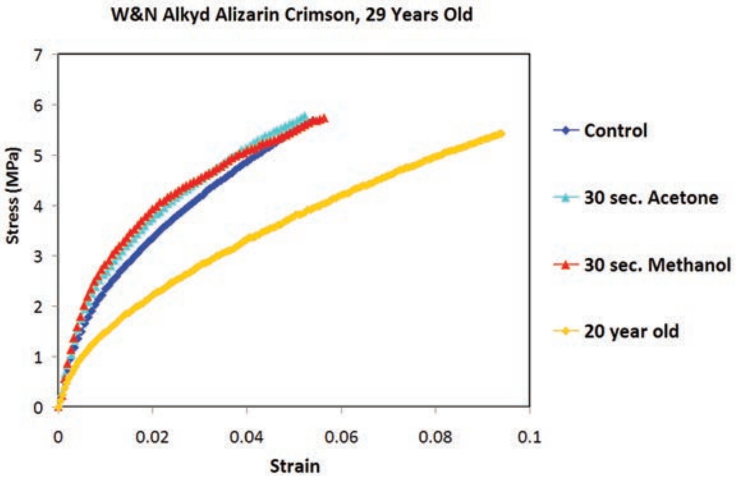

FIGURE 9. Changes in the mechanical properties of an alkyd paint made with alizarin crimson after 20 and 29 years of aging. The effect of solvent exposure of the older paint is also shown. After 29 years of drying the paint is fairly resistant to methanol and acetone.

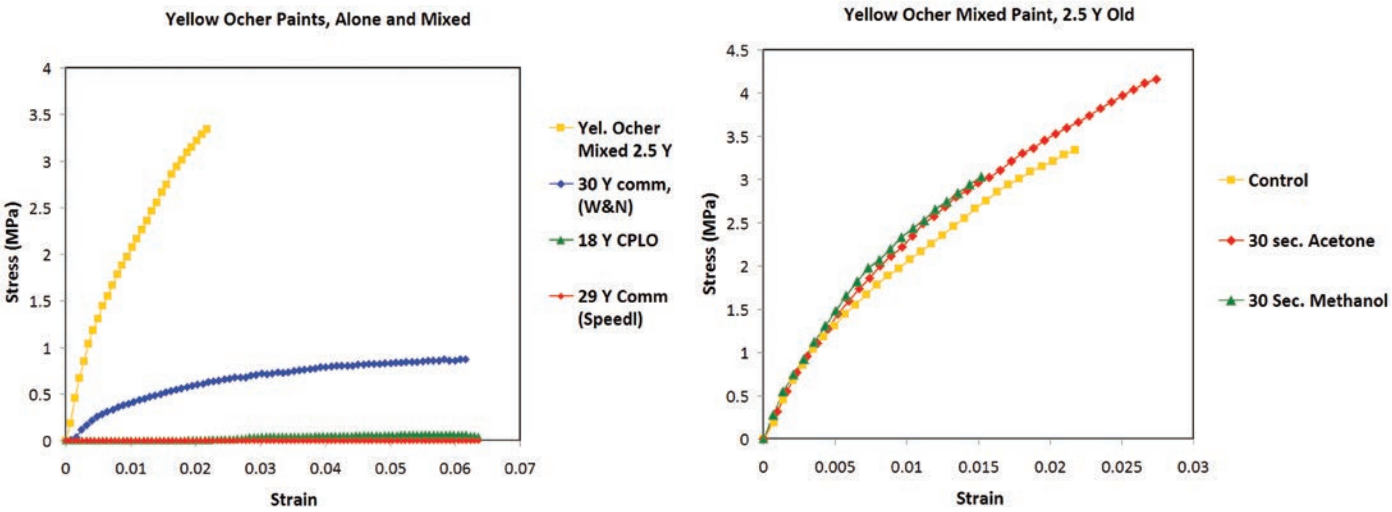

FIGURE 10. (left) Comparison of the mechanical properties of a 2.5-year-old mixed yellow ocher and flake white paint with a pure yellow ocher paint. (right) The effect of solvent exposure on the mechanical properties of the 2.5-year-old mixed yellow ocher paint. After only 2.5 years of drying the paint is fairly resistant to both methanol and acetone.

Figure 10 (right) shows the effects of solvents on the mechanical properties of the 2.5-year-old mixed yellow ocher. There is only a modest degree of stiffening, indicating that unreacted fatty acids were partially removed by the solvents. The paints made with both alizarin and terre verte in cold-pressed linseed oil and mixed with the flake white paint also showed enhanced resistance to solvents.

THE EFFECTS OF ION MIGRATION

Current research suggests that a wide variety of metal ions, apart from the ions mentioned above, affect the ultimate film formation of oil paints. The exact reaction of these ions with the drying oils is not clearly understood, but there is now considerable evidence that some metal ions are not only capable of migrating throughout a given paint layer but sufficiently mobile to migrate from one paint layer to an adjacent paint layer in a painting having multiple layers. In this case, the migrating ions are also capable of affecting the film formation of adjacent paint layers. Unfortunately, this has both positive and negative consequences. On the positive side a painting with a lead white ground has the potential of increasing the durability of all paint layers above the ground. Conversely, paintings with earth grounds do not have the benefit of metal ions contributing to the durability of adjacent layers. Those paintings are typically easily damaged by high environmental moisture levels and cleaning solvents. A layer of paint made with zinc oxide can cause all adjacent paint layers to either

FIGURE 11. Comparison of a 10 s exposure to toluene for (left) an 11-year-old burnt umber on polyester and (right) a 2.5-year-old burnt umber on white lead paint.

become brittle when otherwise they would dry to a tough durable film or alter the drying characteristics of adjacent paint layers to such an extent that "drying cracks" can appear.

In June 2007, six paints (yellow ocher, terre verte, alizarin madder lake, raw Sienna, burnt Sienna, and burnt umber), all ground in cold-pressed linseed oil, were applied over a 16-year-old paint made with basic lead carbonate and cold-pressed linseed oil. The paints were examined after 2.5 years of drying. The first observation that could be made is that the 2.5-year-old paints cast over the white lead paint gained an increased resistance to toluene when compared to the same but older paints cast on polyester films. Figure 11 compares the results of 10 s exposure to toluene on an 11-year-old burnt umber cast on a polyester substrate and a 2.5-year burnt umber cast over the 16-year-old white lead paint. Very similar results were obtained for 10 s exposure to toluene on the yellow ocher, terre verte, alizarin madder lake, raw Sienna, and burnt Sienna cast over the white lead paint. In other words, all of the paints cast over the white lead paint showed a marked increased resistance to the toluene.

X-RAY MICROANALYSIS

In order to confirm that ion migration was occurring in the 2.5-year-old burnt umber paint cast over the 16-year-old lead white paint, X-ray microanalysis was performed on a cross section of this paint. Figure 12 shows the results of this microanalysis, which confirms the presence of lead in the burnt umber layer of paint. It is of interest to note that the iron from the burnt umber did not migrate into the lead paint. Furthermore, spatial simplicity analysis shows that the lead in the white lead paint is lead carbonate, but there is an entirely different lead association forming in the iron bearing burnt umber, as shown in Figure 13.

A multivariate statistical analysis of the hyperspectral X-ray imaging data taken across the burnt umber–white lead interface was performed. Although there are an infinite number of model solutions to such a three-dimensional data cube, the employed

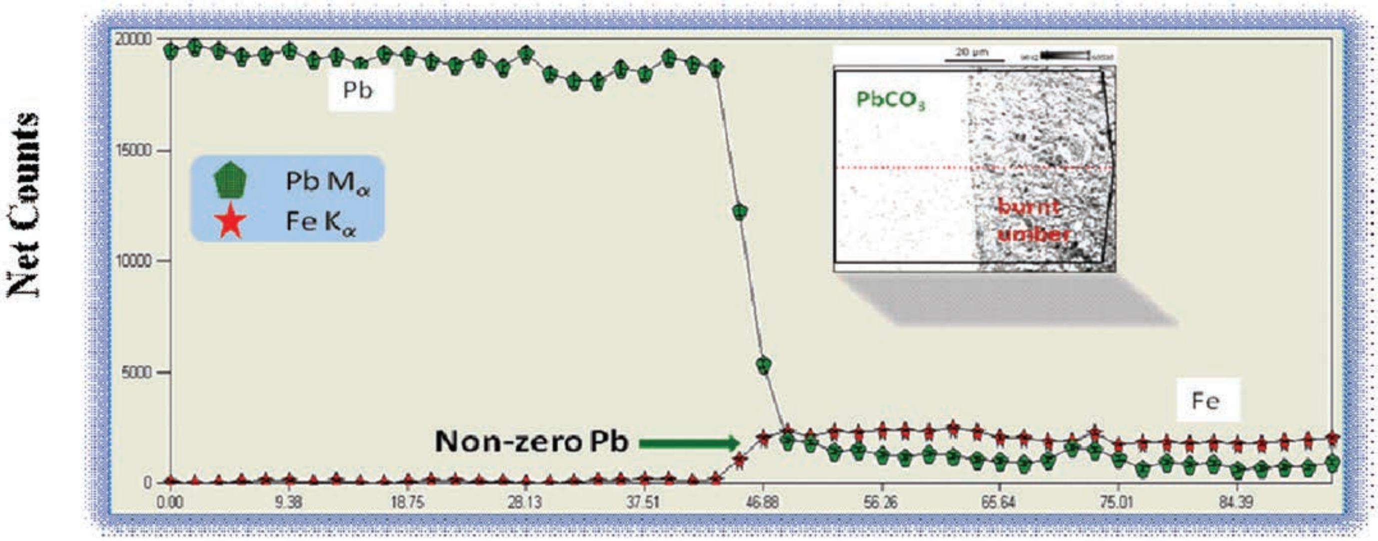

FIGURE 12. The presence of lead in the burnt umber paint is evident, but there is no iron in the lead paint. The inset shows the interface of the two paint layers and the line followed for the analysis.

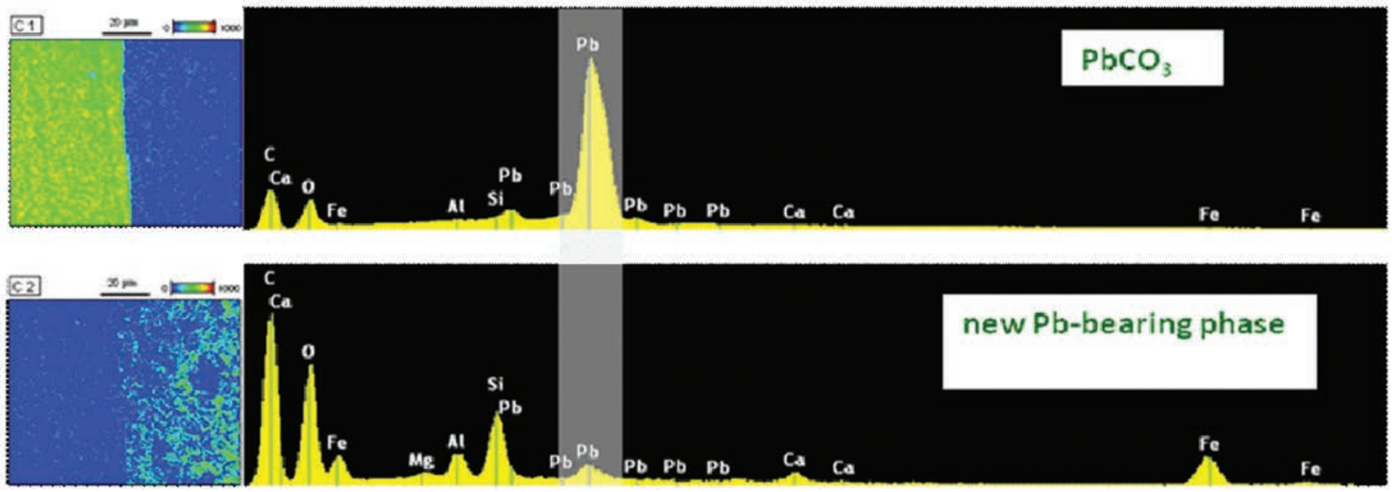

FIGURE 13. (left) Multivariate statistical results approximating the data set by matrix multiplication of pure component concentration images and (right) their spectral signatures. Using a spatial simplicity model, the top image represents $PbCO_3$, and the bottom image corresponds to a new Pb association formed in the umber paint layer (Keenan, 2009).

solution was the one that generates high image contrast in the *X-Y* spatial dimensions (Keenan, 2009). The pure spectral components derived from this analysis include a chemically complex Pb-bearing component rich in C and O as well as containing Mg-Al-Si-Ca and Fe (see Figure 13). The Pb compound extends from the Pb carbonate interface to some tenths of micrometers into the paint layer.

A one-dimensional analysis of the spectral image data additionally supports the presence of Pb well into the paint layer. Integrated net counts (characteristic minus background radiation) for Pb derived from an area at the interface region for the Pb M_a X-ray line are plotted orthogonal to the interface and distinctly show nonzero Pb net intensities within the burnt umber layer (Figure 12).

DISCUSSION

Because lead is not known to be present in burnt umber at any appreciable concentration, an explanation for the Pb-bearing phase within the paint after 2.5 years is best described by cation migration. During the drying process, the basic lead carbonate is apparently solubilized, hypothetically by minor amounts of hydrolyzing oil, at the interface and migrates *via* diffusion into the umber paint layer. The presence of clays in this layer may trap the migrating lead compound to form a spectrally distinct association, as evidenced by the presence of the Si-Al-Mg-Ca. Whether this is merely a physical adsorption, typical of clays, or a new compound that integrates all these elements plus the Pb-Fe-C-O is yet to be determined. Although the exact nature of this phase is currently not known, carbon comprises ~39% (by weight) of its composition, suggesting an oil or fatty acid lead salt plus the ferruginous clay mixture.

The possibility has been considered that the Pb signal detected is an artifact caused by secondary characteristic fluorescence of Pb in Pb carbonate by characteristic Ca and Fe radiation in the burnt umber. However, considering the low concentration of Ca in the paint and the large offset in energies between the Fe *K* line and Pb *M* X-ray lines, these possibilities appear remote. Secondary fluorescence of Pb by continuum radiation in the paint layer is perhaps more likely. However, the distribution of the Pb-bearing phase is not concentrated at the interface and tails- off in intensity as a function of distance, as one might expect if this phenomenon were responsible for producing the Pb spectral signature observed. Moreover, the 1-D profile of Pb net intensities do not decrease sharply as a function of distance from the Pb carbonate interface, further suggesting that evidence for cation migration during the drying process has been established.

CONCLUSIONS

The results obtained from this long term study can be summarized as follows:

- The early drying of oil paints is due to autoxidation, but it does not necessarily result in a tough, durable film.
- The later film-forming processes are largely the result of metal ions from pigments, added driers, or even contamination from other materials inducing cross-linking and polymerization.

- Not all pigments contribute to the development of good paint films, and some, such as zinc oxide, can actually have detrimental effects, causing brittleness and even delaminating the paint layers.
- Pigments such as the earth colors, organic dyes, and blacks fail to induce a durable film, and this is a result of hydrolysis of the paints.
- Without pigments supplying "active" metal ions, film formation in drying oils is poor.
- Different pigments have dramatically different effects on film formation and the durability of both oil and alkyd paints.
- In the competing processes of polymerization, cross-linking, and hydrolysis, hydrolysis can be dominant in paints made with many pigments, including the earth colors.
- Mixing paints made with active pigments can increase the durability of paints with less active pigments.
- One layer of paint in a painting can affect other adjacent layers both positively and adversely. The paint chosen for the ground layer can affect the long-term stability of the painting.

This study has confirmed that ion migration occurs and has shown that this migration may result in the formation of new associations for the case of a burnt umber paint applied over a lead white paint. Research into the ion migration process is just beginning, and far more research is required to elucidate it.

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