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Traditional Oil Paints: The Effects of Long-Term Chemical and Mechanical Properties on Restoration Efforts

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Introduction

Some of the most important cultural icons in the world are oil paintings. Preserving them for future generations requires a fundamental understanding of the long-term chemical, mechanical, and physical behavior of their components. If the properties are understood, modeling and even predicting the effects of exposure to changes in temperature, relative humidity, shock, and vibration are possible.[1,2] Furthermore, if the chemistry and rate of the drying of oil paints is understood, predicting the effects of both structural and cosmetic (cleaning) conservation treatments is possible.

In the late 1980s, the Smithsonian Center for Materials Research and Education (SCMRE), formerly the Conservation Analytical Laboratory (CAL), purchased custom-manufactured oil paints for a research program examining several aspects of oil paint behavior. Thirty-nine different pigments and six different oils were used in mixing the paints. No other fillers, extenders, or driers were added to the paints, which is in marked contrast to commercial artists' oil paints currently manufactured. This restriction was imposed so that the custom-made paints would more closely resemble those used in past centuries. The only consideration was the interaction of pigment and oil. Two of the most pressing questions were how do pigments affect the drying of oil paints, and how long does it take for paint to dry? The latter question held the most interest, in that some conservation research has been done on modern paints up to 10 or so years old in the hope of developing a better understanding of the conservation treatment of paintings and painted surfaces that are hundreds of years old.[3–6] The principal criticism of these experiments was that the paint samples used by these researchers were not old enough to truly represent old paint films. This paint research program was undertaken to study the effects of pigments on the behavior of oils and to determine when the chemical and physical processes of drying reached equilibrium. The determination of the time frame for chemical (oxidation) and physical (mechanical) processes is reported here.

Sample Preparation and Testing

The paints were prepared for drying by uniformly applying them to clear polyester sheets so that, after a period of time, "dry" paint films could be cut and the polyester film backing peeled away. The thickness of a typical paint sample was 0.25 mm. In this way, an unsupported paint sample was capable of being tested for chemical, physical, and mechanical properties. Several hundred paint samples were prepared and tested over the past 10 years. Specimens were weighed periodically with a Mettler balance to 0.1 mg. Tensile tests were performed on miniature screw-driven tensile testers. The average strain rate was a very slow 0.0005 mm/mm per second, to minimize time-dependent behavior. Temperature and relative humidity were kept constant at 22°C and 50%, respectively.

Rates of Oxygen Uptake for Pigmented, Cold-Pressed Linseed Oil

Most of the literature describes the drying of oil paints as a process involving an uptake of oxygen, an intermediate formation of hydroperoxides, and, finally, polymerization. This entire free-radical process is called autoxidation. Oxygen absorption is easily monitored by weighing paint samples over time, the weight change reflecting oxygen uptake minus the loss of some volatile compounds. The weight loss due to evaporation of volatiles is small compared with the oxygen uptake during the first year of drying in a pigmented film. The term "drying" has many meanings, but is taken here to mean stabilization of the oxidative and physical processes over time. Paints made with different pigments absorb differing amounts of oxygen, largely as a result of the amount of oil used in making the paint. Some paints have high pigment-volume concentrations (PVCs) and low oil-volume concentrations (OVCs) and other paints have the reverse. At the same time, the rate of oxygen absorption varies from paint to paint and is a result of the pigment used in the paint. Over time, unpigmented cold-pressed linseed oil increases its weight by about 14% of its initial weight, due to this oxygen absorption. Even after two years, the pure oil is rubbery, tacky, and difficult to handle, suggesting that the drying process is slow. Paints appear to be even slower driers, even though they feel stiffer and less tacky. Chemically, the drying process goes on for years. Much of this apparent perception of "dryness" is a result of the pigmentation of the paint, as the pigment is considerably stiffer than the medium.

Lead carbonate and cold-pressed linseed oil were used to make a traditional white-lead paint having a pastelike consistency typical of artists' paints. The resulting paint has a 44.4% PVC and a 55.6% OVC. The percentage weight of oil for this paint is 15.9%, and the oil component alone is expected to increase in weight by 14% in the drying process. The total weight of the paint sample should increase by 2.25% over a similar drying time. However, the white-lead paint gained only 1.1% in weight after 1.5 yr, as illustrated in Figure 1. Furthermore, after an initial period of about one month, the rate of weight increase settles into a natural log increase, as shown in

Figure 2. When the data are extrapolated into the future, they indicate that the paint will reach the theoretical weight limit only after several centuries. With the exception of a paint made with cobalt-blue pigment and cold-pressed linseed oil, other paints follow a similar behavior as the white lead. The cobalt-blue paint gains weight much more rapidly and appears to reach its maximum limit within decades rather than centuries, as shown in Figures 3 and 4. This paint has a 14.7% PVC and an 85.3% OVC, and 60.6% of the total weight of the paint is from the oil component. The theoretical maximum weight gain for the cobalt-blue paint was 8.48%. It is important to note that the data suggest that the maximum weight gain will be ultimately reached.

Clearly, different pigments can modify the chemistry of drying oil paints, and this can in part explain the lower-than-expected weight gain of the white-lead paint. On the other hand, it can be readily shown that thin surface films form on the drying paints, and these films act as barriers to further oxygen absorption. They also give the illusion that the paint has dried throughout. A slowly but ever-thickening surface film gives rise to slower diffusion and produces the natural log absorption rate observed. Regardless of the explanation, the results of these measurements strongly suggest that some, if not most, oil paints take a very long time to dry (i.e., for their bulk properties to reach equilibrium). If applied paint is very thin, then the paint will give the impression of drying very quickly.

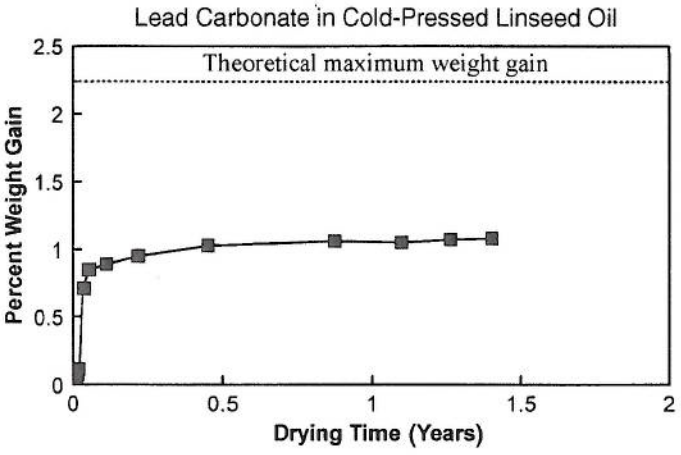

Figure 1. The weight gain of white-lead oil paint with time. There is an initial rapid weight gain due to oxygen absorption for about one month, after which the weight increase is very slow. The theoretical maximum weight gain is the expected weight increase of the oil component alone.

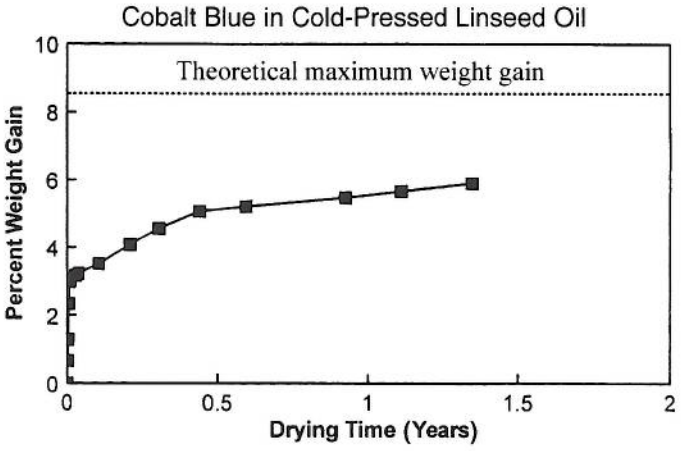

Figure 3. The weight gain of cobalt-blue oil paint with time. There is an initial rapid weight gain up to about one month, after which the weight increase slows but is much more rapid than that of white-lead paint. The theoretical maximum weight gain represents the expected weight increase of the oil component alone.

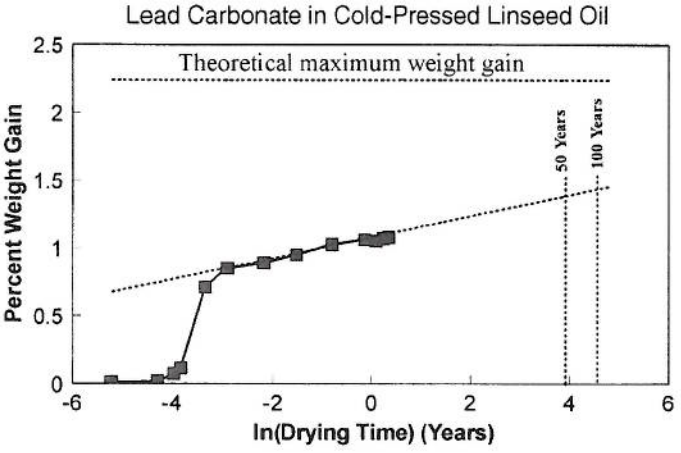

Figure 2. The weight gain of white-lead oil paint plotted against the natural log of the drying time. Once the early initial and rapid weight gain is completed, the rate follows the natural log plot quite linearly. The dashed lines indicating the points of 50 yr and 100 yr are included to provide references to the length of time required for the paint to completely gain the weight expected. The data indicate that centuries are required for the paint to completely gain the maximum weight.

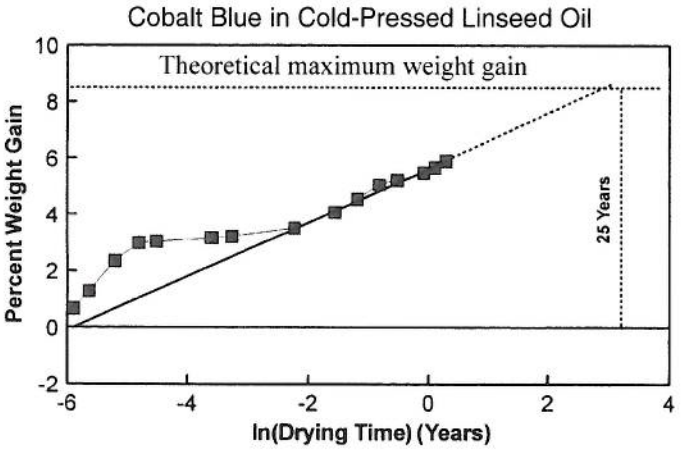

Figure 4. The weight gain of cobalt-blue oil paint plotted against the natural log of the drying time. Once the early initial and rapid gain is completed, the rate follows the natural log plot quite linearly. The dashed lines indicating a point at 25 yr is included to provide reference to the length of time required for the paint to reach the weight expected. In contrast to the white-lead paint, the data here indicate that it will take a little less than 25 yr for the paint to reach the maximum weight.

Mechanical Tests and Observations over Time

As a paint polymerizes during drying, it becomes stiffer and stronger. The stiffness and strength of the paint can be measured using mechanical testing methods. Increased stiffness means that the paint sample requires more force (stress) for the same amount of elongation (strain). The strength of the paint is the highest stress reached, and in this case, this occurs when the sample breaks. Since the paint samples are unsupported films (not bonded to substrates), tensile testing yields the strength of this paint directly. The rate of any increase in stiffness can be used to obtain a further and independent measure of the rate of drying of paints. The same white-lead paint described earlier in this article will be used to illustrate some points, although the same behavior was observed in several other paints, including titanium white in cold-pressed linseed oil and some commercially prepared white paints containing different oils.

The tests were conducted after the paint was allowed to dry for 0.184 yr, 0.269 yr, 0.98 yr, and 10 yr in a controlled indoor environment typical for artists' paintings.

Figure 5 illustrates the results of the tensile tests of the white-lead paint and the age of each test specimen. Also in this figure are vertical dashed lines (lines of constant strain) that intersect the stress–strain plots. As can be seen, for any value of strain, the stress increases as the paint samples age.

The information shown in Figure 5—time, stress, and strain—can be re-plotted on a time versus stress plot, as shown in Figure 6. In this figure, while the stress is shown to increase over time for any given strain, the rate of this stress increase diminishes with time. Also in this figure are the values of the breaking stresses over time, which initially rise, but then start to level out. This suggests that there is a maximum stress level for the paint that is reached before the paint is completely dry. The rate of stress increase or stiffening of the paint with time can be more clearly shown when the natural log (ln) of time is used instead of linear time for the ordinate of the plot.

Figure 7 shows that all of the data beyond the very early stages of drying (three months) plot as linear functions of the ln of time. Even more useful is the potential to extrapolate the data (dashed lines) to extended periods of drying time and examine the possible long-term results of drying. All of the vertical lines on Figure 7 represent lines of constant drying times. The stresses indicated by the intersection of the lines at constant drying times and the lines of constant strain can be used to construct the expected stress–strain plots of the paint film in the future.

The information provided in Figure 7 was used to reconstruct the stress–strain plots of white-lead paint at 1 yr and 10 yr, and this is shown in Figure 8. Also shown in Figure 8 are the predicted stress–strain plots for the paint at 50 yr, 100 yr, and 250 yr. The theoretical strength of the 50-yr-old paint sample is estimated to be at a maximum at approximately 3.7 MPa. The strengths of the 100- and 250-yr-old paints are shown to be less, since it is known that the stiffer (the older) the paint, the more prone to fracture it will be. Figure 8 suggests that while there is a significant difference between the 1-yr-old paint and the 50-yr-old paint (which is about 2.6 times stiffer), there is only predicted to be about a 20% increase in stiffness between the 50- and 250-yr-old paints.

If the projected stress–strain behavior shown in Figure 8 has validity, it suggests—at least for white lead in cold-pressed linseed oil—that the drying time is very long, and the paint continues to stiffen and perhaps become brittle after several centuries. The projection also suggests that a paint that does not have considerable flexibility at the 1–2-yr drying stage will in fact become very brittle over time. Solvent tests conducted on paints less than 20–25 yr old leach out a considerable amount of low-molecular-weight materials, embrittling the paint film. This should not be confused with aging or drying effects. Another result is that attributing the increases in stiffening of the paint to chemical degradation processes may also have little meaning, since an old paint gets stiffer naturally without additional chemical interactions. What remains to be determined is the natural rate of processes such as hydrolysis and what impact these processes have on the mechanical properties of paint.

On the other hand, if the paint drying process stops sooner than the projections suggest, then the paints will dry to more flexible films than anticipated in the long run. In many respects, the projected plots

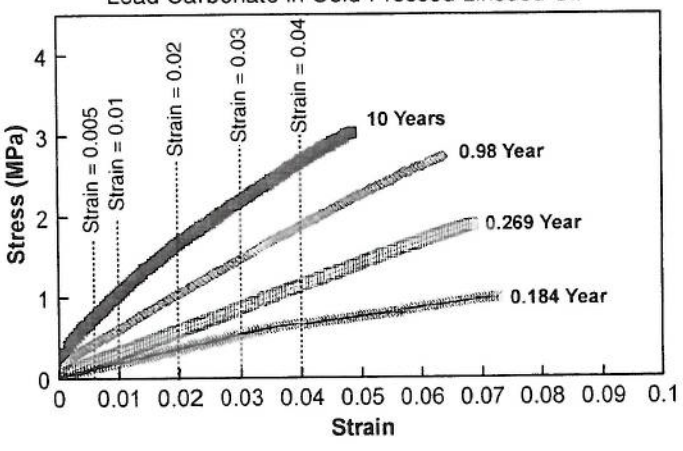

Figure 5. The stress–strain results of white-lead oil paint tested at different time intervals and under identical test conditions. The vertical dashed lines are lines of constant strain, and the stress of the paint at these constant strains increases with time. This indicates that the oil polymerization is continuing and is not completed during this test period; that is, the paint is not "dry" after 10 yr.

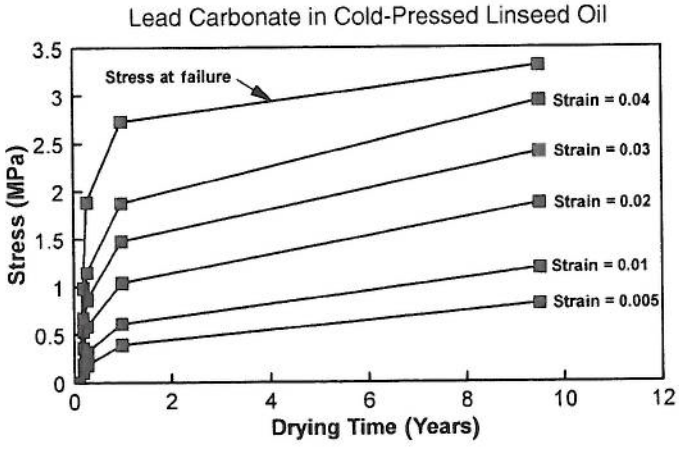

Figure 6. The plots of the paint stresses at constant strains plotted against the drying time of the paint. After 10 yr, while the rate of the stress increase is diminishing, the stresses are clearly still rising. This paint has not dried after 10 yr. The breaking or failure stress is still rising, but at a lower rate of increase than the stresses at the fixed strains. This suggests that the strength of the paint will reach a maximum before the paint is fully dried.

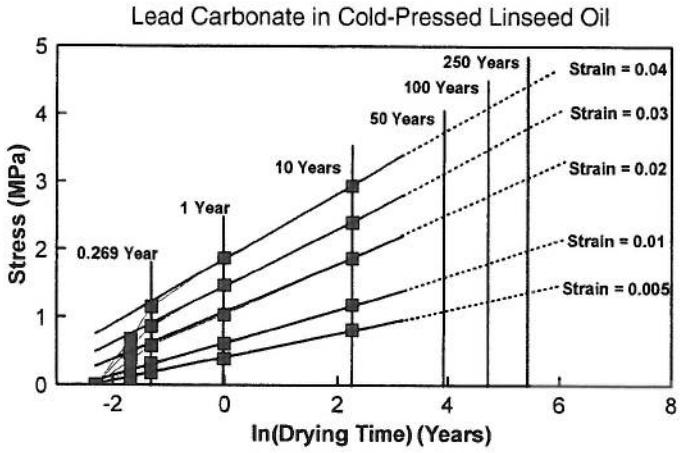

Figure 7. The plots of the paint stresses at constant strains plotted against the natural log of the drying time of the paint. After an initial drying period of about three months, the data show a linear stress increase. This suggests that the drying of the paint is an ongoing process with ever-diminishing stress increases. The data also suggest that the behavior of the paint can be projected into the future, and the stresses are clearly still rising. This paint has not dried, even after 10 yr. This information allows one to predict the stress–strain behavior of this paint into the future.

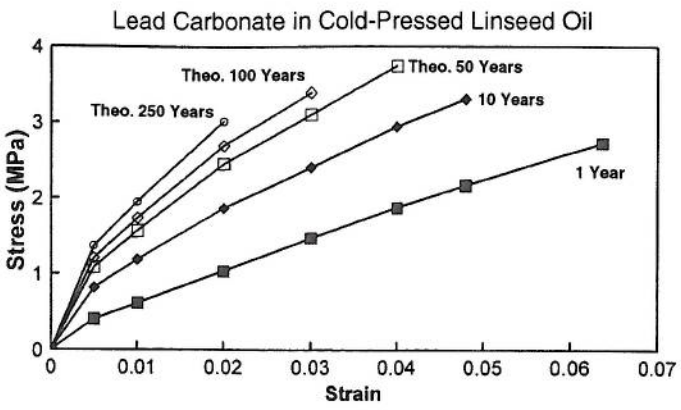

Figure 8. The stress–strain plots for white-lead paint at 1 yr and 10 yr and the predicted stress–strain plots for the future (50 yr, 100 yr, and 250 yr). The plots suggest that the paint continues to stiffen over long periods of time as a result of the natural drying processes alone.

represent a conservative approach, in the sense that this is the most severe expectation.

Clearly the data indicate that chemical and physical processes are going on that will take decades, if not centuries, to complete. A lack of understanding of these chemical and mechanical drying processes of traditional oil paints has led to potentially damaging conservation treatments, particularly when cleaning solvents are used. The results of this research program suggest that great care must be taken in the modeling of cleaning methods, conservation treatments, and environmental effects if recently prepared paint samples are used in experimental testing. This presents difficulties in forming models for conservation treatments and confuses the issue of whether natural aging or previous treatment is responsible for the present condition of many paintings.

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PRESERVING ART THROUGH THE AGES

MRS NEWS

ABSTRACTS

DEPARTMENTS

ON THE COVER: Through materials research, conservation scientists can gain a greater understanding of historical artifacts and the craftmanship used to create them. Modern techniques such as synchrotron x-ray analysis can shed light on the internal microstructure of objects such as the 16th-century astrolabe pictured here. Superimposed on the astrolabe is a pinhole diffraction pattern obtained from this particular artifact, showing the random arrangement of the polycrystalline grains in the brass plate, the pattern of which is consistent with manual hammering techniques used to work brass in the 16th century.
See the technical theme that begins on p. 13.
Cover montage by Mary Ann Forys, Argonne National Laboratory.