

The Changing Mechanical Properties of Aging Oil Paints

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ABSTRACT

The stiffening and embrittlement of oil paints over time has been a real concern for those responsible for the long term care and preservation of paintings. This paper examines the effects of time, pigments, relative humidity (RH), temperature and solvents on the mechanical properties of traditional oil paints. In this way it is possible to determine the role of each factor in causing the paints to become brittle. Even after 14 years the oil paints show little evidence that the long term "maturing" processes have begun to slow down. It is shown that there seems to be little correlation between the time paint requires to "dry-to-the-touch" and the longer term mechanical properties. Both low and high temperature levels can increase the stiffness of the paints though the mechanisms are quite different. Considerable hydrolysis of the paints occurs early in their history and the ones that hydrolyze most quickly are the ones that remain the most flexible.

INTRODUCTION, THE EARLY DRYING STAGES OF PAINTS MADE WITH DRYING OILS

The chemistry of the drying of oil paints is a complex, multi-step process in which oxygen is absorbed, unsaturated ester hydroperoxides are formed, and then the hydroperoxides decompose with subsequent cross-linking. This process called auto-oxidation has been extensively reviewed [1-10]. In the process of absorbing oxygen, the paint initially gains weight and simple weighing over time allows one to follow the early stages of the drying process. Figure 1 illustrates the weight gain of four different paints made with lead carbonate ground in cold pressed linseed oil, cold pressed safflower oil, walnut oil, and poppy seed oil over a 20 day period.

Within this period of time a thin tack free film forms on the surface of the paint. The time to form this film is one definition of the "drying time." Each of the oils has a different "dry to the touch" period and the letter D placed on each of the plots indicates that time. For example, the paint made with the cold pressed linseed oil takes 16 days while the paint made with the walnut oil takes only about three days. The weight plots level out at that time indicating that a rather impervious film has formed and oxygen penetration is thus limited. The inability of the paint to absorb easily additional oxygen slows the drying of the paint below the surface film. Within about three years, however, most but not all paints having a thickness of about 0.25mm or less will form a cohesive film throughout its thickness. It is what happens beyond those three years that is of interest.

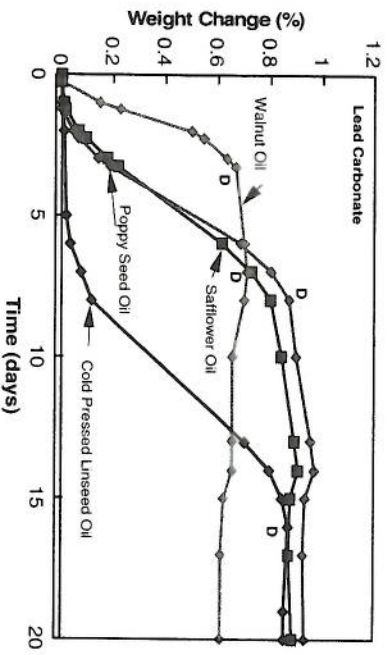
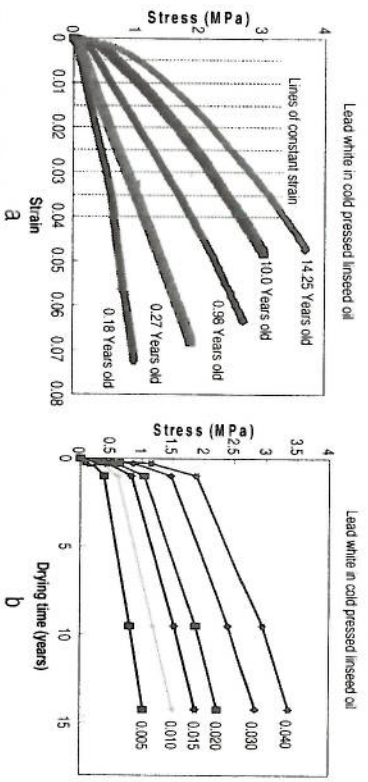


Figure 1. The percent weight gain of oxygen versus time for paints made with basic lead carbonate and four different drying oils. The points labeled "D" are the times where the surface of the paints became "dry to the touch." At these points the surface film reduced the uptake of oxygen.

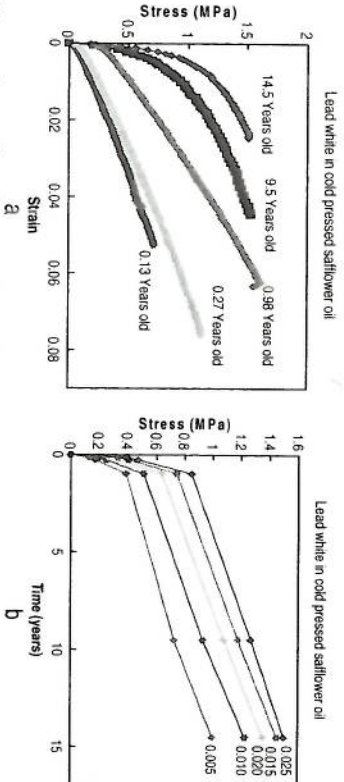
THE MECHANICAL BEHAVIOR OF PAINTS MADE WITH DRYING OILS

The conventional perception is that paints made with drying oils become brittle over very long drying times. In this context the term brittle means that the paint film becomes quite stiff and will break when subjected to very small deformations. This is in marked contrast to paint films that remain very flexible over long periods of time. Here the term flexible means that paint will distort or "stretch" a long way before breaking. The terms brittle, flexible, and force are terms that relate to the mechanical properties of the paint and they can be accurately quantified. Mechanical testing can be used as another way to track the drying or stiffening behavior of paint films over long periods of time. The stiffness of paint is usually calculated from the initial slope of the stress-strain plot. This is usually referred to as the modulus of elasticity. Several hundred paints were manufactured for the Smithsonian Center for Materials Research and Education (SCMRE) and all of the paints tested and discussed in this paper were cast on polyester film and allowed to dry for the stated period of time. What should be noted is that the paints were cast and stored at the commonly accepted museum environment of 40% to 50% RH and 23° C. The polyester film was removed prior to testing and the tests are of free, unsupported paint films. All of the tests were conducted at the same strain rate and after the paints had fully equilibrated to the environmental conditions indicated. Figure 2a shows the tensile stress-strain tests of a paint made by grinding basic lead carbonate in cold pressed linseed oil. This paint would be typical of a paint made several hundred years ago and without the addition of any modern driers, stabilizers, or inert bulking material. As shown in this figure, the paint is getting stronger (greater stress at break) as the time of drying continues, and there is a modest reduction in the strain (stretch) at the point of failure. The strain levels in these tests are fairly high and this paint is still quite flexible after 14.25 years of drying. One point of interest is that the paint shows a continual increase in



Figures 2a and b. Figure 2a shows the stress versus strain plots of basic lead carbonate paint made with cold pressed linseed oil at different ages. Figure 2b shows the stress at constant strains versus time for basic lead carbonate paint made with cold pressed linseed oil. These plots indicate that the processes that cause the increase in stiffness and strength show little indication of slowing down. This means that whatever chemical processes affect the mechanical properties of this paint are still continuing.

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proportional to time elapsed. There is only a suggestion that the rates of stress increase are diminishing. It will take additional drying time to develop a better picture of the long term behavior but it is quite clear that this paint is still undergoing changes in mechanical properties, even after 14 years. This paint is not unique in that the continued changes are occurring over a long period of time. Figure 3a shows the tensile test conducted over time of basic lead carbonate ground in cold pressed safflower oil. As with the lead white in cold pressed linseed oil, this paint shows a general increase in strength and a decrease in the strain to break. Figure 3b plots the stress increase at constant strain over the drying time for the lead white in safflower oil. This paint behaves in a nearly identical manner as the lead white in cold pressed linseed oil and shows considerable flexibility after 14.5 years.

PAINTS WITH OTHER PIGMENTS

All of the different paints cast and tested require varying times to form tack free surface films and there are considerable differences in the mechanical properties after drying for long periods of time. Figure 4 shows some representative stress-strain plots for paints made with cold pressed linseed oil and tested after drying between 12.25 and 14.5 years at 40%-50% RH and 23° C.

The yellow ochre and raw umber paints (earth colors) can be described as extremely flexible with practically no strength. Both paints contain iron oxide and clays. They develop very little strength yet they both form tack free films in four to five days, considerably faster than the paint made with basic lead carbonate. The malachite paint contains copper compounds and requires only four days to form a tack free surface film. It is flexible but not as strong as the basic lead carbonate paint. The paint made with titanium dioxide has some stiffness but little strength, yet it took only a little more than a

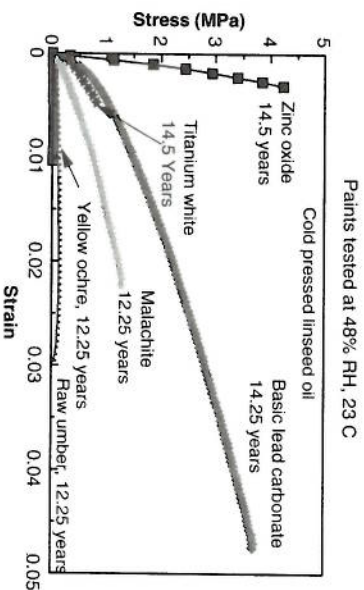


Figure 4. The stress versus strains of paints made with six different pigments and cold pressed linseed oil. The paints range in stiffness from extremely low and flexible (yellow ochre and raw umber) to extremely brittle (zinc oxide). There is no correlation between the mechanical behavior of the paints and the time required to dry tack free.

single day to form a tack-free surface film. The paint made with the zinc oxide can truly be described as brittle, requiring little elongation to break it. While it can develop extremely brittle behavior in as little as three years, it takes at least 22 days to form a tack free film. Brittle behavior is of real concern for paints containing zinc oxide. It is routinely added as a secondary pigment to currently manufactured artists' paints that are labeled titanium white, lead white, and to a multitude of light paints called hues. These paints often become very brittle in as little as three years if excessive zinc is used. It makes some sense to add some zinc oxide pigment to the titanium dioxide in an effort to give the mixture some strength but it does slow the "dry-to-the-touch" time of the titanium dioxide paints. Verdigris, another copper pigment produces a very brittle film. Interestingly, gamboge is a resin that dissolves in the oil and yields an extremely brittle oil-resin varnish.

It might be noted for drying oils and the large number of paints examined at this lab that there seems to be very little correlation between the times required to form tack-free surface films and the mechanical properties of the film. There seem to be very different processes acting after the initial drying. With some exceptions, the paints in general tend to increase in both stiffness and strength. If the plot for the zinc white paint shown in Figure 4 represents the maximum stiffness that any paint can achieve, then extrapolation of the basic lead carbonate data indicates that 150 to 180 years will be needed to reach that point at the same proportional rate of increase in the mechanical properties. If the rate of change of properties slows down even a small amount then it will take centuries, if ever, for the basic lead carbonate to paint become as stiff as the zinc oxide paint.

THE HYDROLYSIS OF PAINT

One of the proposed explanations for the embrittlement of paint is hydrolysis [11]. Hydrolysis is the reaction of water with the glyceride esters of the oil, whether cross-linked as a polymer or not. The freed fatty acids can react with metal ions to produce soaps. Chemical analyses of these paints showed that over time there is an increase in the hydrolysis of the paint and soap formation. This certainly can offer an explanation of the changes in the mechanical properties. However, if one looks at the mechanical properties and the degree to which paints are hydrolyzed, that correlation really doesn't seem to exist. Several paints were analyzed to determine the degree to which these paints were hydrolyzed. The methods of analysis were described previously [13]. Table 1 below shows the results of the chemical analyses and compares them to the modulus of the paints. As seen in this table, hydrolysis can be extensive early in the paint history and in general the greater the hydrolysis the lower the modulus of the paint. In other words, hydrolysis appears to correlate with greater flexibility in oil paints made with cold pressed linseed oil not brittleness. If one detects brittleness in old paints, then an explanation other than hydrolysis must be found.

Table 1. Percent of hydrolysis of fatty acids in paints made from cold pressed linseed oil.

Paint	Age (years)	Azelaic	Palmitic	Stearic	Modulus
Raw umber	12.25	72%	81%	87%	5 MPa
Red iron oxide	12.25	69%	83%	83%	5 Mpa
Malachite	12.25	25%	42%	44%	89 MPa
Titanium dioxide	14.5	38%	69%	67%	140 MPa
Basic lead carbonate	14.75	8.8%	33%	32%	300 Mpa
Zinc oxide	14.5	2.3%	15%	11%	1667 MPa

Some of the hydrolysis of the paints results in the formation of soaps when metal ions are present. Table 2 shows the percent of hydrolyzed paint that is soap. Unlike the total amount of hydrolysis, there seems to be no correlation between soap formation and the stiffness of the paint.

Table 2. The percent of soap formation in the tested paints made with cold pressed linseed oil.

Paint	Age (years)	Azelaic	Palmitic	Stearic	Modulus
Raw umber	12.25	2.9%	3.4%	2.2%	5 MPa
Red iron oxide	12.25	4.8%	1.9%	1.4%	5 Mpa
Malachite	12.25	4.6%	1.7%	0.6%	89 MPa
Titanium dioxide	14.5	9.6%	3.3%	2.2%	140 MPa
Basic lead carbonate	14.75	6.6%	1.9%	0.9%	300 Mpa
Zinc oxide	14.5	1.9%	4.4%	2.6%	1667 MPa

SOLVENT EXTRACTION

Some of the paints described earlier were subjected to solvent extraction by immersion in acetone for 24 hours to determine the amount of extractable material as drying times increased. After 24 hours immersion the paints were dried and then allowed to equilibrate at 48% RH and 23° C. They were then weighed. This weight is a measure of the amount of soluble low molecular weight polymeric materials as well as soluble fatty acids and soaps. In general these materials can act as plasticizers. The results of these extractions are shown in Table 3.

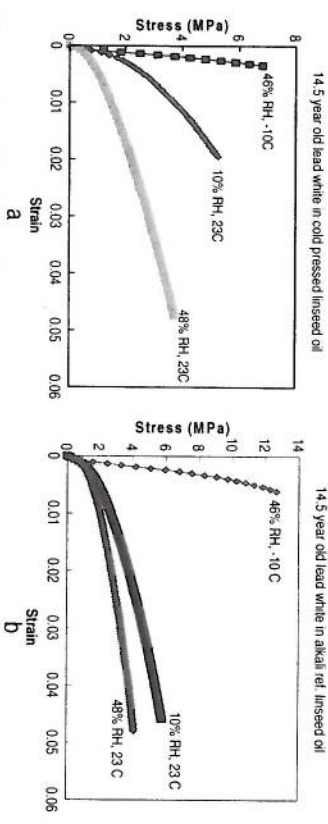
Table 3. Percent extractable material using acetone.

Paint description	Drying time (years)	Extractable material (%)
Zinc white in cold pressed linseed oil	14.5	2.78
Lead white in cold pressed linseed oil	14.5	3.71
Lead white in alkali refined linseed oil	14.5	4.04
Lead white in acid refined linseed oil	14.5	3.68
Lead white in cold pressed safflower oil	14.5	3.61
Malachite green in cold pressed linseed oil	12.25	4.55
Titanium white in cold pressed linseed oil	14.5	11.92
Raw umber in cold pressed linseed oil	12.25	Disintegrated
Red iron oxide in cold pressed linseed oil	12.25	Disintegrated

The amount of material extracted from the paint films gives an indication of the amounts of low molecular weight compounds present in the film. The more extractables present, the more unpolymerized or partially polymerized materials that act as plasticizers are present. The percent of extractable material test also gives one an excellent sense of the effect of cleaning solvents on the durability of applied paints. The earth colors completely disintegrated during exposure to the solvent. It is widely known that the earth colors and other dark colors are very sensitive to damage by cleaning solvents.

THE EFFECTS OF TEMPERATURE AND HUMIDITY

Temperature and relative humidity (RH) can cause paints to become brittle in different ways. Low temperature can have immediate consequences on the durability of paint films. Paint films are similar to many other polymers in that they pass through a phase change as the temperature is decreased. This is sometimes called the glass transition temperature or T_g and in oil paints this region is between -10°C and -20°C . Higher temperatures take longer to produce stiffening through different mechanisms often evaporation of plasticizers. While low temperature embrittlement can be reversed by raising the temperature, high temperature alteration of the mechanical properties is permanent. Figures 5a, 5b, and 6 show three oil paints tested at three different environmental conditions, 48% RH and 10% RH at 23° C and -10° C at 46% RH. Figure 5a shows the test results of basic lead carbonate in cold pressed linseed oil at these three environments. The first observation is that paints tested at low temperature become glassy and lose all flexibility. Low temperatures cause most of the cracking that one observes in paintings and painted surfaces [12]. At 10% RH the lead white paint becomes somewhat stiffer and stronger, but still retains a considerable amount of flexibility. The effects of low temperature on the mechanical properties of oil paints are much more drastic than RH changes can cause.



Figures 5a and b. Figure 5a shows stress versus strain plots of lead carbonate paint made with cold pressed linseed oil. The tests were conducted at three different environments, 48% RH, 23° C; 10% RH, 23° C; and 46% RH, -10° C. While lower humidity did increase the stiffness and strength of the paint, it was the low temperature that caused the paint to become extremely brittle. Figure 5b shows the stress versus strain plots of a basic lead carbonate paint made with alkali refined linseed oil. The tests were conducted at three different environments, 48% RH, 23° C; 10% RH, 23° C; and 46% RH, -10° C. While lower humidity slightly increased the stiffness and strength of the paint, it is at low temperatures that the paint becomes extremely brittle.

In Figure 5b is shown basic lead carbonate (lead white) in alkali refined linseed oil tested in the same three environments as the previous lead white in cold pressed linseed oil. Low temperature causes the paint to become quite brittle. On the other hand, low relative humidity seems to have only a small effect on the mechanical properties of this paint. It is worth commenting that alkali refined linseed oil is used extensively in the manufacture of artists' oil paints today.

Figure 6 shows the tensile tests of zinc white in cold pressed linseed oil in three different environments. Included in this figure are the test results of basic lead carbonate for comparison purposes. At 48% RH, 23° C the zinc white paint is already extremely brittle and the change in relative humidity down to 10% has almost no effect on the mechanical properties. Cooling the paint down to -10° C increases the stiffness only slightly without affecting the strength. It is possible that zinc white paint represents the extremes of physical properties that paints can achieve since it is so little affected by either low relative humidity or low temperature. Zinc white pigmented oil paints become extremely brittle as soon as they dry and remain so as they age.

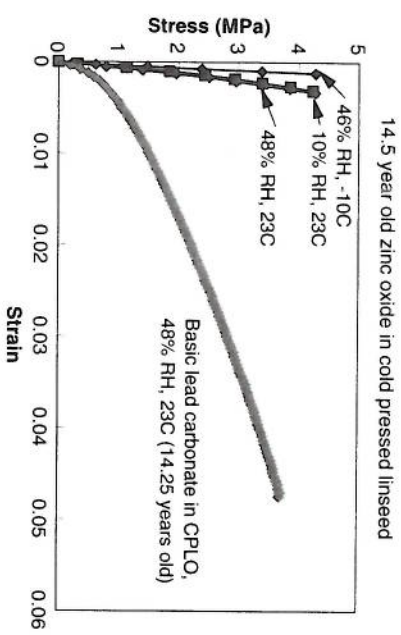
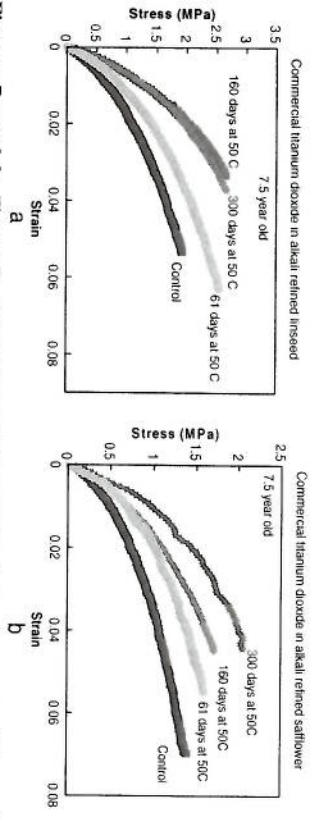


Figure 6. The stress versus strain plots of zinc oxide paint made with cold pressed linseed oil. The tests were conducted at three different environments, 48% RH, 23° C; 10% RH, 23° C; and 46% RH, -10° C. The zinc oxide paint is so brittle that neither the lowering of the RH or the temperature made a significant difference in the mechanical properties of this paint. The stress versus strain results of the lead carbonate paint made with cold pressed linseed oil are shown for comparison purposes.

THE EFFECTS OF MODEST ELEVATED TEMPERATURES

Modest levels of heat can stiffen paints over time. Commercially prepared "titanium whites" ground in alkali refined linseed oil and alkali refined safflower oil were exposed to 50° C (122° F) for long periods of time. This is the temperature that one might find in an attic where there is no environmental control. Samples were periodically removed from the oven and allowed to equilibrate to 50% RH and 23° C after which they were mechanically tested. This particular paint is a successful mixture of titanium dioxide and zinc oxide that retained considerable flexibility at room temperature after 7.5 years of drying. Figure 7a shows the results of testing the "titanium white" ground in the linseed oil. The paint tends to stiffen with continued exposure to the heated environment. However, after 160 days of exposure there is no further increase in the stiffness. The 160 day sample and the 300 day sample show nearly identical results. Even after 300 days of exposure to 50° C this paint retains a considerable amount of flexibility. On the other hand the "titanium white" ground in alkali refined safflower oil showed continued stiffening over the duration of the heat tests. Figure 7b shows the mechanical test results of this paint. The results show that the longer the exposure (at tests up to the 300 days of the study) the greater the stiffness of the paint. Nevertheless the paint still retained considerable flexibility.

While elevated temperatures can certainly increase the rate of chemical processes are responsible for the increased stiffness of paints over time, unreacted fatty acids do act as plasticizers to the paints and can be volatilized by the heat [13]. It is most likely a

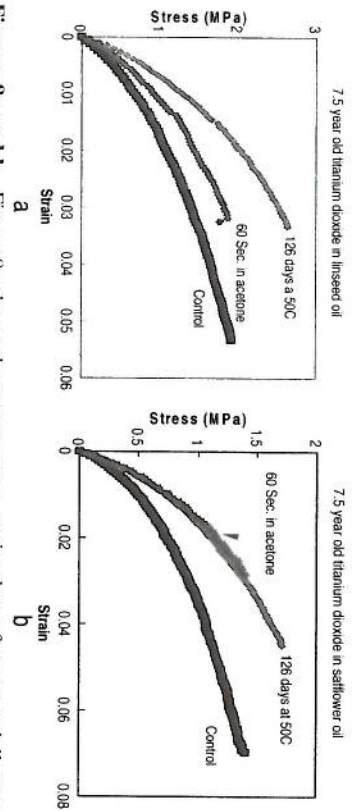


Figures 7a and b. Figure 7a shows stress versus strain plots of commercially made "titanium white" paint made with alkali refined linseed oil. This paint contains a small proportion of zinc oxide pigment. The tests were conducted at 48% RH and 23° C after the paint had been exposed to 50° C for different periods of time. Figure 7b shows the stress versus strain plots of commercially made "titanium white" paint made with alkali refined safflower oil. This paint contains a small proportion of zinc oxide pigment. The tests were conducted at 48% RH and 23° C after the paint had been exposed to 50° C for different periods of time. In both cases time at elevated temperatures increases the stiffness and strength of the paint.

combination of this volatilization and other factors that cause the stiffening of the paints subjected to elevated temperatures.

THE EFFECTS OF SHORT TERM EXPOSURE TO ACETONE ON THE MECHANICAL PROPERTIES

The same commercially mixed "titanium whites" used in the heat exposure tests were used to test the effects of short term exposure to acetone. Acetone is a solvent that is commonly used in the removal of old varnishes from paintings. The paint films were 0.25 mm thick and can be considered "thick" films. The paint samples were immersed for 60 seconds, then dried and allowed to equilibrate to 50% RH and 23° C prior to conducting the mechanical tests. Figure 8a shows the difference in the mechanical testing results of the "titanium white" in linseed oil before and after the 60 second exposure to acetone. Included in the results for comparison purposes is the result of the test of heating for 126 days at 50° C. As can be seen, even a very short exposure to acetone increases the stiffness of the paint but not as much as the 126 days of exposure to the heat. Additional difference in the mechanical testing results of the "titanium white" in safflower oil before and after the 60 second exposure to acetone. Included in the results for comparison purposes is the result of the test after 126 days at 50° C. For this paint, the acetone increased the stiffness to the same degree as the paint sample that was heated to 50° C for 126 days. The acetone treated paint lost strength in comparison to the heated paint.



Figures 8a and b. Figure 8a shows the stress versus strain plots of commercially made "titanium white" paint made with alkali refined linseed oil. This paint contains a small proportion of zinc oxide pigment. The tests were conducted at 48% RH and 23° C after the paint had been exposed acetone for 60 seconds and allowed to thoroughly dry. Figure 8b shows the stress versus strain plots of commercially made "titanium white" paint made with alkali refined safflower oil. This paint contains a small proportion of zinc oxide pigment. The tests were conducted at 48% RH and 23° C after the paint had been exposed acetone for 60 seconds and allowed to thoroughly dry. The short term exposure increases the stiffness and strength of both paints.

CONCLUSIONS

The mechanical properties of oil paints are affected by a number of factors. The properties of a paint after it has "dried" (several years) are determined primarily by the composition of the paint, especially the type of pigment. Different pigments in the same oil can produce paints that range from weak and extremely extensible, to strong and flexible, to stiff and brittle even under "ideal" environmental conditions. If paints are aged under "normal" conditions, their properties change slowly over time. It is predicted that a typical paint such as lead white pigmented linseed oil will require many centuries, if ever, to become "brittle". Exposure to cold environments results in immediate increases in stiffness and brittleness, but this effect lasts only as long as the paints are maintained at low temperature. Exposure to solvents (as short as a minute or so) also results in increases in brittleness, but through a different mechanism (extraction of low molecular weight material) that results in permanent changes. High temperatures also result in permanent increases in brittleness through loss of low molecular weight material but through volatilization. This is a longer-term process (weeks or months) at temperatures as low as 50° C, although higher temperatures (such as might be encountered in a fire) will produce changes even more rapidly. The hydrolysis over time of ester linkages in oil paints has been proposed as a cause of embrittlement, but no such correlation was found. If anything, paints that hydrolyzed most quickly were those that were and remained the most flexible. The long term properties of paints (including their susceptibility to hydrolysis) are determined very early in their life. Paints that are "brittle" either became

brittle very early in the aging process or were exposed to extreme environmental conditions or overexposure to solvents.

REFERENCES

1. Wexler, H., 'Polymerization of Drying Oils', *Chemical Reviews*, 64 (1964) 591-611.
2. Mills, J.S. and White, R., *The Organic Chemistry of Museum Objects*, Butterworths, London, 1987, 30-35.
3. Baeman, L., 'Olefin Oxidation', *Quarterly Reviews* 8 (1954) 147-167.
4. Russell, G. A., 'Fundamental Processes of Autoxidation', *Journal of Chemical Education* 36 (1959) 111-118.
5. Mills, J. S., 'The Gas Chromatographic Examination of Paint Media. Part I. Fatty Acid Composition and Identification of Dried Paint Films', *Studies in Conservation* 11 (1966) 92-107.
6. Mayo, F. R., 'Free-Radical Autoxidation of Hydrocarbons', *Accounts of Chemical Research* 1 (1968) 193-201.
7. Hutchinson, G. H., 'Some Aspects of Drying Oils Technology', *Journal of the Oil and Colour Chemists' Association* 56 (1973) 44-53.
8. Porter, N. A., 'Mechanisms for the Autoxidation of Polyunsaturated Lipids', *Accounts of Chemical Research* 19 (1986) 262-268.
9. Chan, H. W.-S., 'The Mechanism of Autoxidation' in *Autoxidation of Unsaturated Lipids*, ed. H. W.-S. Chan, Academic Press, London (1987) 1-16.
10. Porter, N. A., Caldwell, S. E. and Mills, K. A., 'Mechanisms of Free Radical Oxidation of Unsaturated Lipids', *Lipids* 30 (1995) 277-290.
11. Jorrit, D.J. vanden Berg, Klaas Jan vanden Berg, and Jaap J. Boon, 'Chemical Changes in Curing and Aging Oil Paints', ICOM Committee for Conservation, Preprints from the 12th Triennial Meeting, Lyon, Volume I, (1999) 248-253.
12. Mecklenburg, M.F., McCormick-Goodhart, M., and Tumosa, C. S., 'Investigation into the Deterioration of Paintings and Photographs Using Computerized Modeling of Stress Development', *JAIC* 33(1994) 153-70.
13. Erhardt, D., Tumosa, C.S., and Mecklenburg, M.F., "Natural and Accelerated Thermal Aging of Oil Paints," *ICC, Traditions and Innovation, Advances in Conservation*, Contributions to the Melbourne Congress, (2000), 65-69.
14. Tumosa, C.S., Millard, J., Erhardt, D., and Mecklenburg, M.F., "Effects of Solvents on the Physical Properties of Paint Films," ICOM Committee for Conservation, Preprints from the 12th Triennial Meeting, Lyon, Volume I, (1999) 347-352.

Linseed Oil Paint as Ionomer: Synthesis and Characterization

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ABSTRACT

As linseed oil ages, hydrolysis and oxidation produce acid groups on the polymer chain that may lead to ionic behavior. The effect of these changes is difficult to determine in old paints because of the lack of records of environmental and treatment histories that can alter the physical properties significantly. A series of paints were made that have chemical properties similar to those of aged paints and that mimic old paints. Their properties seem to show flexibility as well as coherency but low strength and a high susceptibility to solvents.

INTRODUCTION

The term ionomer was originally introduced in 1964 by Dupont to indicate a thermoplastic polymer containing both covalent and ionic bonds [1]. This definition now includes other ion-containing or ion-linked polymers. As linseed oil based paints age, it has been postulated that they become ionomers as the paints hydrolyze and produce pendant carboxylic acid groups that react with metal ions from pigments to form ionic carboxylate salts. The characteristics of such an ionomeric film were not measured [2,3].

Linseed oil is a mixture of fatty acid esters of glycerin, mostly unsaturated 18 carbon carboxylic acids with two and three double bonds and small amounts of saturated fatty acids as well. Autoxidation occurs on exposure to air, producing a crosslinked solid film. Autoxidation has been extensively reviewed [4-6]. The transformation of the covalent linseed oil film to an ionomeric film can proceed through at least two mechanisms. First, oxidation of the unsaturated fatty acid ester groups at the C9 double bond position can lead to early formation of the diacid, azelaic acid. The azelaic acid is still attached to the polymer by the original ester group while the newly formed, and pendant, carboxylic acid group is capable of reacting with metal ions. Second, sequential hydrolysis of the three ester linkages of the glycerin esters can lead to one, two and finally three carboxylic acid groups, most of which are linked to the crosslinked fatty acid polymer matrix of the dry film through bonds formed during the drying process. Free glycerin is also formed as the alcohol byproduct of the hydrolysis. Because both the oxidation and hydrolysis reactions occur in the context of a pigmented film (paints), the presence of the pigment must be taken into account. The ability of metal ions from pigments, particularly lead, to become mobile in the oil matrix has been known for some time [7]. For inorganic pigments the ability of the pigment particles to release metal ions or form complexes at their surface partly determines the character of the ionomer, although in regard to the polymer, the number, spacing, and ratio of ionized groups to metal ions is the dominant effect [8]. Since the pigment will be in considerable excess relative to the oil, even if the metal ion

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