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

REFERENCES


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 ionomic 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 Du Pont 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 carbonate salts. The characteristics of such an ionomic 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 ionomic 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 polymeer 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
can react with more than one carboxylate group, the probability is that each metal ion will bond to only one carboxylate group and not create any crosslinks or bridged structures [9]. This limits the crosslinking phenomenon and affects the mechanical behavior. The first descriptions of ionomers indicated that stiffness and tensile strength increase with increasing acid content and neutralization by metal ions [1].

Unaltered samples of old, naturally aged paints in a form that can be tested mechanically are essentially impossible to obtain. The alternatives are to age paints by accelerated ageing or to create “aged” paints synthetically. Accelerated ageing has problems that have been addressed previously [10,11]. The other approach is to create paint films with structural alterations that reproduce the chemistry and physical behavior of old paint films. This is the approach we have taken. The present experiments were performed to determine the chemical and physical nature of ionic microstructure films derived from linseed oil.

MATERIALS AND METHODS

To prepare the hydrolyzed oil, 500 grams of cold pressed linseed oil were stirred overnight with a slight molar excess (0.1 l) of 10% (w/w) potassium hydroxide in methanol. Excess 3M hydrochloric acid was added, and an acidic pH verified with pH paper. Dichloromethane was added to extract the free acids. Water (200 ml) was added to help break up the partial emulsion that formed. The dichloromethane solution was separated in a separatory funnel, a second dichloromethane extract was added to the first, and the dichloromethane was removed in a rotary evaporator under partial vacuum in a warm (approximately 30°C) bath. The resulting slightly reddish mixture lost no weight immediately when cast as a thin film, indicating no dichloromethane remained. Gas chromatography showed that the mixture was >99.5% free fatty acids with less than 0.5% monoglycerides, indicating that the hydrolysis was essentially complete. The oil was stored in the dark under nitrogen gas until used.

Aliquots of the hydrolyzed oil were added to the original cold pressed oil to give final concentrations of 25, 50 and 75% hydrolyzed oil in cold pressed linseed oil. Five oils were then available for testing ranging from the original cold pressed unhydrolyzed oil to 100% hydrolyzed oil. These oils were milled with appropriate quantities of various pigments to achieve a “buttery” consistency. The paint was then drawn in strips on a polyester film and dried in a laboratory at 40-50% RH and 20°C. The paints all had similar densities, 1.70 g/cc. The paints were tested after 3.75 years. This was considered enough time for the major initial drying process to be substantially complete [11]. The drying of the red iron oxide paint prepared with the hydrolyzed oil was monitored by infrared spectroscopy. The paint lost the unsaturated -C=C-H band at ~3010 cm⁻¹ indicative of the near completion of the reaction of the unsaturated bonds with oxygen [12,13]. Lead white, verdigris and red iron oxide paints showed the presence of a carboxylate peak as well at 1520, 1605 and 1624 cm⁻¹ [14].

Drying curves were determined using a previously described technique [15]. Mechanical testing was performed using screw driven tensile testers as described previously [16].

Specimens were typically 6 mm x 130 mm x 0.3 mm. A 30 second stress relaxation was allowed between data points to limit time dependent behavior. Infrared spectroscopy was performed with a Mattson Polaris system Fourier transform infrared spectrometer (FTIR) equipped with a microscope attachment. Spectra were obtained at 8 cm⁻¹ resolution.

RESULTS

A series of red iron oxide paints were prepared from cold pressed oil added to hydrolyzed oil to give concentrations of 25%, 50% and 75% hydrolyzed oil as well as 100% hydrolyzed and, as a control, cold pressed oil alone. In addition, raw umber, lead white, ivory black, smalt and verdigris paint films were prepared in 100% hydrolyzed oil as well with the paints cast as films on polyester sheets. All of the paints dried as coherent films that remained attached to the sheets and sometimes developed motting about the surface. Infrared analysis showed these areas to contain a higher concentration of saturated fatty acids indicative of “livering” formed from partially hydrolyzed oil and basic pigments [17] or from too high a percentage of free fatty acids. The paint made from the cold pressed linseed oil dried to the touch in six days, the totally hydrolyzed paint dried in only three days. It may be that the method of preparation of the hydrolyzed oil removed antioxidants normally present in small quantities in minimally processed oils. Stress-strain tests were then performed on several paint films using screw driven tensile testers. Figure 1 shows the stress-strain plots for the series of red iron oxide paints ranging from the control with 0% hydrolyzed oil, up to 100% hydrolyzed oil paints. The overall impression of the data is that as the amount of hydrolyzed oil increases, the stiffness, strength and extensibility decrease significantly as seen in figures 2 and 3.

Figure 1. The graph shows the stress-strain plots for the series of red iron oxide paints ranging from the control (0%) hydrolyzed oil, to 100% hydrolyzed oil paints with decreases in the stiffness, strength and extensibility.
Figures 2 and 3. Plots of the breaking strains and breaking stress (strength) of the paints in figure 1 against the amount of hydrolyzed oil. The data show clear trends in both loss of extensibility and loss of strength with increasing amounts of hydrolyzed oil.

**SOLVENT EXPOSURE BEHAVIOR**

Solvent testing was performed to examine the coherency of the paint films and to evaluate what might happen to such paint films during cleaning. Specimens were tested in acetone, toluene, hexane and de-ionized water by immersion of the free film in beakers. The films were examined over the period of immersion up to 30 minutes. Table 1 summarizes the behavior of the red iron oxide paints. The unhydrolyzed film behaved like a "young" paint, i.e. little change in coherency after immersion. The solvent did extract low molecular weight material and the exposed films were brittle. The 25% hydrolyzed oil mixture behaved similarly, but the 50% mixture shows signs of loss of coherency. These should correspond to moderately aged paint films since 25 to 50% hydrolysis can occur in 10 to 25 years [2,11]. Strong solvents, acetone and toluene, cause the 75% and 100% hydrolyzed paints to disintegrate, leaving a powdery residue. Water had no effect on the coherency of the paints.

**Table 1. Effect of Solvents on Coherency of Red Iron Oxide Paint Films**

<table>
<thead>
<tr>
<th>Composition of paint film</th>
<th>Composition of paint film</th>
<th>Acetone</th>
<th>Toluene</th>
<th>Hexane</th>
<th>De-ionized water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unhydrolyzed paint film</td>
<td>retained coherency</td>
<td>retained coherency</td>
<td>retained coherency</td>
<td>retained coherency</td>
<td>retained coherency</td>
</tr>
<tr>
<td>25% Hydrolyzed</td>
<td>retained coherency</td>
<td>retained coherency</td>
<td>retained coherency</td>
<td>retained coherency</td>
<td>retained coherency</td>
</tr>
<tr>
<td>50% Hydrolyzed</td>
<td>disintegrated with pressure</td>
<td>coherent but tacky</td>
<td>retained coherency</td>
<td>retained coherency</td>
<td>retained coherency</td>
</tr>
<tr>
<td>75% Hydrolyzed</td>
<td>disintegrated with pressure</td>
<td>disintegrated with pressure</td>
<td>retained coherency</td>
<td>retained coherency</td>
<td>retained coherency</td>
</tr>
<tr>
<td>100% Hydrolyzed</td>
<td>disintegrated with pressure</td>
<td>disintegrated with pressure</td>
<td>retained coherency</td>
<td>retained coherency</td>
<td>retained coherency</td>
</tr>
</tbody>
</table>

Table 2 shows the solvent behavior of the other five paints made with the hydrolyzed linseed oil. Raw umber, ivory black and smalt pigmented films disintegrated in acetone and toluene. All paints maintained coherent films when exposed to hexane and de-ionized water. In water and acetone the Verdigris partially dissolved to give the characteristic blue color of copper salts. The lead white pigmented paint suffered the least damage on immersion. Even acetone did not disrupt the integrity of the film.

**DISCUSSION**

Mixing untreated and totally hydrolyzed oils prior to mulling with pigment gave oils with varying proportions of unsaturated free acids. The use of a totally hydrolyzed oil to create mixtures, rather than using a partially hydrolyzed oil, may be considered problematic since the step by step partial hydrolysis of oils (fresh or dried) produces mixtures of free acids, mono, di, and triglycerides (or their polymers). The totally hydrolyzed oil, though, should accurately mimic very old oils and the smooth progression of properties from unhydrolyzed to 100% hydrolyzed indicates that using mixtures of fresh and unhydrolyzed oil gives a valid indication of the effects of hydrolysis. Free fatty acids may also accelerate the autoxidation of the oil mixtures leading to a more rapid ageing [18]. The pigmented films were aged at 40 to 50% RH and 23°C in the laboratory for 3.75 years before testing. Infrared analysis showed that the reactive double bonds had disappeared and that soaps had formed as in the normal ageing of paint films.

The properties of the red iron oxide paints vary smoothly with increasing proportions of hydrolyzed oil. The stiffness, strength and extensibility all decrease with increasing hydrolysis. This is somewhat unexpected since it has been postulated that increased ionic character would result in increased stiffness and strength [2]. This is not borne out by the data for the iron oxide paints that show decreasing stiffness and strength. Solvents also affect the paint films, causing embrittlement and increased stiffness and in extreme cases total disintegration of the films. Crosslinking may continue to occur during long term ageing, but only as a minor reaction since the functional groups primarily involved in
crosslinking are used up in the initial drying of the paint. It may be that the supposed increases in stiffness and brittleness in older paints arise from solvent treatments or extreme environmental conditions such as heating rather than the “normal” ageing and hydrolysis of the paints.

Total hydrolysis of the paint films is an extreme condition, but unless solvents are used to remove soluble material, the films remain coherent and will adhere to a substrate. Even the 100% hydrolyzed films retain a breaking strain great enough to survive moderate (~15%) environmental changes in RH, although their resistance to improper treatment and handling is greatly reduced.

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