Focus:

Reactivity of earth and synthetic pigments with linseed oil

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Introduction

The reaction of earth and synthetic pigments with lipidic binders (drying oils, egg yolk,...) has been reported by numerous authors.1,2,3,4,5

 Generally, the formation of metallic soaps by the reaction of the pigments with the free fatty acids in binders has been assumed. Such metallic soaps are likely to act as driers, accelerating the drying and polymerization of the binder.

 Usually, and without much verification, pigments such as white lead, umber, ochre, zinc oxide or manganese brown are said to accelerate the drying of the binders and provide a hard and resistant pigmented film.

 The synthesis of metallic soaps and their use as drying agents has been commonplace; thus the Pb, Mn, and Co soaps are used as driers in industrial paints and artists’ colours.7

 However, there has been no systematic study of the reactivity of the mineral pigments used in industrial paints and artists’ colours.

 Only two works8,9 have dealt with the topic, although not directly. The first studied the variation of the photo-oxidation of linseed oil in the presence of various pigments, and its conclusions are difficult to interpret. The second studied the reactivity of egg yolk and linseed oil by infrared spectroscopy, and the formation of metallic soaps is inferred.

 In a previous work, the study of the reactivity of fats with different compounds in the surface of ancient paints was presented. The reactivity of some compounds (white lead, alumina, gypsum, alums, calcium carbonate...), although in a collateral way, and not specifically referring to pigments, were studied.

 The present work contains a systematic study of the reactivity of a great number of earth and synthetic pigments that have been used throughout the centuries in industrial paints and artists’ colours.

 Study

 The reactivity of a total of 30 pigments was proved. These were supposed to react with linseed oil, either because there were bibliographical references of a possible acceleration of drying or due to their structure (oxides, basic salts, carbonates, acetates,...), which could suggest a possible reactivity.

 The pigments that appear in Table 1 were selected for the study in this way. The pigments that, according to the bibliography, accelerated the reaction of drying are marked with “#”. The remainder were chosen because of their structure.

 Table 1: Selection of pigments

| # | White lead | Cadmium yellow |
| # | Sulfate white lead | Cassel yellow |
| # | Zinc white | Zinc yellow |
| # | Zinc sulfate | Calcium chromate |
| # | Bismuth white | Molybdate |
| # | Red ochre | Venetian |
| # | Sienna | Cobalt green |
| # | Red lead | Azurite |
| # | Umber | Cobalt blue |
| # | Manganese brown | Carbolan blue |
| # | Yellow ochre | Manganese blue |
| # | Litharge | Copper blue |
| # | Naples yellow | Cobalt blue-green |
| # | Chrome yellow | Manganese black |
| # | Chrome orange | Cobalt black oxide |

(No reactive pigments, according to the bibliography)

 The composition and structure of these pigments1,2,3,4,11 appear below:

 White lead: Basic lead carbonate. In the White lead pigment the main compounds are: 2PbCO3.Pb(OH)2; 4PbCO3.2Pb(OH)2.PbO and PbCO3.

 Sulfate white lead: Lead sulfite and basic lead sulfite. PbSO4, PbSO4.PbO and PbSO4.3PbO.

 Zinc white: Zinc oxide. ZnO.

 Zinc sulfide: Zinc sulfide (wurtzite form). ZnS.

 Bismuth white: Basic bismuth nitrate. OBiNO3.H2O.
Red ochre: Ferric oxide (synthetic). Fe₂O₃.
Sienna: Natural earth.
26 - 80 % Fe₂O₃; 9 - 64 % aluminates and silicates, 8 - 14 % H₂O.
Red lead: Lead oxide.
Pb₃O₄ (85 - 99 %) + PbO (1 - 15 %).
Umber: Natural earth.
Fe₂O₃·3H₂O, MnO₂ and sodium, potassium and calcium silicates and aluminates.
Manganese brown: Manganese oxides and hydroxides.
MnO·H₂O, MnO, MnO₂·H₂O.
Yellow ochre: Hydrated ferric oxide (synthetic).
Fe₂O₃·H₂O.
Litharge: Lead monoxide.
PbO.
Naples yellow: Lead orthoantimonate or pyroantimonate:
Pb₃(SbO₄)₄ or Pb₅Sb₂O₇.
Chrome yellow: Lead chromate.
PbCrO₄.
Chrome orange: Basic lead chromate.
PbO·PbCrO₄.
Cadmium yellow: Cadmium sulfate.
CdS.
Cassel yellow: Basic lead chromate.
PbCrO₄.
Zinc yellow: Zinc - potassium chromate.
znO·K₂O·4CrO₃·3H₂O.
Calcium chromate: Neutral calcium chromate dihydrate.
CaCrO₄·2H₂O.
Malachite: Basic copper carbonate.
Cu₂O·Cu (OH)₂.
Verdigris: Basic copper acetate.
Cu(CH₃COO)₂·2Cu(OH)₂.
The neutral acetate: Cu(CH₃COO)₂ has been found also in verdigris.
Cobalt green: Cobalt zincate.
CoO·ZnO.
The pigment treated is CoO·ZnO.
Azurite: Basic copper carbonate.
2CuO·Cu (OH)₂.
Cobalt blue: Cobalt aluminate.
CoO·Al₂O₃.
Cerulean blue: Cobalt stannate.
CoO·SnO₂.
Manganese blue: Barium manganate with barium sulfate.
BaMnO₃·BaSO₄.
Copper blue: Copper hydroxide.
Cu(OH)₂.
Cobalt blue-green: Cobalt chrome - aluminate.
Al₂O₃·Cr₂O₃·3CoO.
Manganese black: Manganese dioxide.
MnO₂.
Cobalt black oxide: Cobaltous - cobaltic oxide.
Co₂O₃·(Co₂O₃·CoO).

The pigment samples received the treatment indicated in experimental section. The extraction with chloroform-ethanol permits the recovery of the unreacted linseed oil and the metallic soaps, when formed.

Metallic soaps present characteristic absorption bands in the IR spectrum between 1570 and 1650 cm⁻¹, which are not present in the treated linseed oil.

Results
The production of metallic salts of the fatty acids consists in the simple replacement of the hydrogen of the carboxyl group with a metal. This can be accomplished in several ways, eg, by the action of a base (hydroxide or oxide) on a fatty acid; by double decomposition of a soluble salt of a fatty acid and a salt of a mineral acid, or by saponification of glycerides or other esters of fatty acids with a base or metallic oxide.

Many special soaps (driers) are produced from fatty acids by the action of bases or oxides on the free acid or by double decomposition reactions. Driers which are manufactured for use in preparing paints, varnishes, enamels, and other protective coatings, are of three general types which are designated as kettle-cooked, fused, and precipitated. In the kettle-cooked type of drier, metallic salts or oxides such as lead oxide or acetate, manganese oxide or borate, cobalt acetate, zinc oxide, calcium oxide or hydroxide are generally heated (200 - 380°C) with oils, primarily linseed oil. The oxides or salts split the glycerides and react with the acid residues to form fatty acid salts.

The fused type of driers are prepared by reacting fatty acids with metallic oxides or salts to form the corresponding salt of the fatty acid.

The IR spectra of the extraction residues of each one of the following tested pigments are all the same and equal to the attached spectrum (Figure 1), corresponding to the linseed oil heated at 125°C for 24 hours (Figure 1).

Figure 1: Linseed Oil heated for 24 hours at 125°C.

<table>
<thead>
<tr>
<th>Non reactive pigments</th>
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<tbody>
<tr>
<td>Sulfate white lead</td>
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<tr>
<td>Zinc sulphide</td>
</tr>
<tr>
<td>Red ochre</td>
</tr>
<tr>
<td>Sienna</td>
</tr>
<tr>
<td>Umber</td>
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<tr>
<td>Manganese brown</td>
</tr>
<tr>
<td>Yellow ochre</td>
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<tr>
<td>Chrome yellow</td>
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<tr>
<td>Chrome orange</td>
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</table>

Since no metallic soaps were detected it is therefore reasonable to deduce that these pigments do not react with linseed oil.

The IR spectra of the residues of the remaining pigments tested that do react to form metallic soaps, and the possible causes of this reactivity are presented.

a) White Lead (Figure 2)
The band between 1611 - 1490 cm⁻¹ (maximum at 1556 cm⁻¹) is identified with the carboxylate ion of the lead soap formed.