WEIGHT CHANGES ON OXIDATION OF DRYING AND SEMI-DRYING OILS

CHARLES S. TUMOSA AND MARION F. MECKLENBURG

Smithsonian Center for Materials Research and Education, 4210 Silver Hill Road, Suitland, Maryland 20746-2863

Abstract.—Objects in ethnographic and ancillary natural history collections contain many types of vegetable oils as components of varnish coatings, paints and lubricants. Tests were performed on thin oil films dried in a laboratory environment. These oils, composed of the glycerol esters of unsaturated fatty acids, will oxidize through a free radical process and crosslink to form polymers of variable properties. Oxygen uptake produces an initial weight gain but further oxidation yields compounds such as carbon dioxide, and short chain acids, aldehydes, ketones and alcohols that can volatilize and contribute to a loss of weight. Monitoring weight changes can provide information on the duration and magnitude of these reactions. Weight changes are greatest in the first year and are still detectable up to two years later. Acid or base processing of the oils affects the incubation period for oxygen uptake but not the long term weight change behavior. Weight loss can be quite dramatic depending on the oil composition. Oils with low linoleic acid content eventually lose more weight than linseed oil and even a non-drying oil with high oleic acid content, olive oil, is surprisingly active after two years. In addition to the chemical effects, changes in weight also indicate alteration of the physical and mechanical properties of the oil films.

INTRODUCTION

Objects in ethnographic and ancillary natural history collections may contain vegetable oils as components of varnish coatings, paints and lubricants, whether originally applied or the result of conservation or restoration. These oils are composed primarily of the glycerol esters of unsaturated fatty acids. They react with oxygen through a free radical process to form hydroperoxides, which in turn decompose and then crosslink to form polymeric gels. This process is called autoxidation and has been covered thoroughly in reviews (Bateman 1954, Russell 1959, Weiser 1964, Hutchinson 1973, Porter et al. 1995). Weight changes are a measurable and an inevitable consequence of the autoxidation processes. Oxygen uptake increases the weight of the oil as hydroperoxides are formed while bond cleavage produces volatile oxidation byproducts such as carbon dioxide, and short chain acids, aldehydes, ketones and alcohols. These diffuse out, volatilize and decrease the weight (Hancock and Leeves 1989). The measured weight changes represent the net change in weight of the oil film due to oxygen uptake during the free radical and polymerization process and the diffusion and loss of volatiles created by oxidation and molecular rearrangements. This behavior was first observed in the 19th century and reviewed early in the 20th century (Weger 1899, Sabin 1911, Eibner 1920). However, only certain oils, notably linseed but occasionally poppy and walnut, were tested and the weight changes were not monitored continuously for periods beyond one or two months. The changes in weight over periods of time other than that required for gelling or becoming dry to touch were not followed in any detailed fashion. Most of such testing was conducted in an industrial or commercial context, and the primary emphasis was on short term changes rather than changes occurring on a museum timescale.

Measurements of the weight changes with time show the continuing nature of
the chemical process and the plots provide information such as the presence and length of the incubation period, the maximum weight gain, and the loss of volatiles after gelling. The length of the incubation period for oxygen uptake is a function of oil processing, presence of antioxidants, or the presence of driers, whether natural or added. The maximum amount of weight gain gives a measure of the amount of crosslinking through oxygen uptake. The removal of chemical compounds as volatiles produces a mass loss and will alter the mechanical properties and diffusion behavior. Weight plots can be altered by the addition of certain metal salts and by metal substrate effects (Morley-Smith 1957). These types of data can be used to investigate oil and paint interactions with substrates.

This paper studies the drying behavior of three types of processed linseed oil commonly encountered in collections and adds new data for five other oils. Safflower, sunflower, walnut and poppy oils were selected because these have been used as substitutes for or additives to linseed oil to reduce the yellowing of white or light colored paints. Olive oil was selected as an example of a common non-drying oil. The effect of copper as a drier on the chemistry of linseed oil was also confirmed using a small amount of copper and an untreated oil. The weight changes over a two year period were monitored to determine activity within the films.

**Materials and Methods**

Test specimens were made from oils representative of those found in collections. These included cold-pressed linseed oil, acid and alkaline refined linseed oils, olive, cold-pressed safflower, refined poppy, cold-pressed walnut and refined sunflower oils. The oils were obtained from Kemper Pigmints, 228 Elizabeth Street, New York, NY 10012 USA. Olive oil was a commercial cooking product. Cold pressed linseed oil with 0.1 percent copper(II) was prepared by adding copper(II) hydroxide to slightly warmed linseed oil and stirring until dissolution was complete. Neat oils were applied to aluminum coupons and held in place by surface tension resulting in gelled films from 0.13 to 0.26 mm (0.005 to 0.010 in) in thickness. Effects of metal substrates were determined in a similar manner using mechanically cleaned copper and lead foils.

Weight changes were monitored using a Mettler model AT201 balance measuring to 0.1 milligrams. The laboratory environment was maintained between 40 and 50 percent relative humidity and 18° to 20°C throughout the study and reflects the environment of most museums. Light was from fluorescent lights, which mimicked natural light, and from indirect natural light. Metal concentrations in oils were determined by inductively coupled plasma mass spectrometry (ICP-MS) using standard techniques (Hill 1999).

**Results and Discussion**

Weight changes in the oils were not immediate and started only after an incubation period when the retardation of the free radical oxidation process by naturally occurring antioxidants was finally overcome. The chemical processing of oils removes these antioxidants and, on testing, the oxygen uptake, as measured by weight increase, starts earlier even though the rate of oxygen uptake is about the same. This phenomenon is evident in Figure 1, which shows the weight change plots of the three types of processed linseed oil over a 45 day period. A
cold-pressed oil, which contained naturally occurring antioxidants, took longer to begin its weight gain (oxygen uptake) but after it started eventually attained the same weight increase as the alkali refined oil. The acid refined oil reached a somewhat lower value as a maximum weight gain. Historically, paints have been made from cold pressed oils, but at present commercial artists’ oil paints that use linseed oil are made with alkali refined linseed oil. Much like a pigmented oil film, the pure oil films reach a “dry-to-touch” state at the point of maximum weight uptake.

Figure 2 shows the longer two-year behavior of these same oils. The trend in the data shows the rapid initial weight increase from oxygen uptake and then a weight loss due to loss of volatiles. After about one year the weight loss starts to level off and by two years there are only minor differences among them although the weight loss continues. The differences in behavior for these three oils are apparent only in the early initial stages and are not significant at later times.

Figure 3 shows the short term weight change for cold-pressed linseed oil in comparison to five other oils—olive, safflower, sunflower, poppy and walnut. The oils show varying incubation periods because of the differences in natural antioxidants and in processing. Figure 4 shows the same oils over a longer two-year period. With the exception of olive oil, the oils are drying oils, i.e., they form gels on oxidation. Their weights decline steadily for about a year and the weight of the oxygenated gel eventually becomes less than the original weight of the oil even after an initial oxygen uptake of ten percent by weight or more. This indicates that the decrease in weight due to the loss of volatiles is greater than weight.
Figure 2. Changes in weight over 700 days of three linseed oil films: unprocessed cold pressed linseed oil, acid and alkali refined oils.

Figure 3. Changes in weight over 45 days of five oil films compared to cold pressed linseed oil. See text for oil preparation.
increases due to oxygen uptake. The degree of weight loss is dramatic for the oils substituting for linseed oil when compared to the linseed oil itself.

Seed oils contain the glycerol esters of fatty acids: principally, two saturated acids—palmitic and stearic; and three unsaturated acids—oleic with one carbon-carbon double bond, linoleic with two double bonds and linolenic with three double bonds. Oxidation may occur directly at the double bonds or through per-oxyl formation at the allylic position. In any case, all three unsaturated acids form azelaic acid, a 9 carbon dicarboxylic acid, on oxidation at the double bond nearest the carboxyl group while other more volatile compounds may be formed from other unsaturated sites. Olive oil contains mostly oleic acid with small amounts of linoleic acid and does not “dry”. Oxidative scission of its single carbon-carbon double bond yields the diacid, azelaic acid, and a 9 carbon saturated acid. By this same mechanism linoleic and linolenic acids similarly form azelaic acid but also smaller more volatile compounds from the other double bond sites if crosslinking does not prevent or inhibit the oxidation at these sites. Oleic acid can also be oxidized biologically and under certain conditions gives hydroxy or oxo saturated acids and can even produce the saturated analog stearic acid by a hydrogenation mechanism (Yan et al. 2001). This chemical route may not be important in the usual chemistry of coatings but may be quite important in archaeological materials, i.e., those buried in moist soils or immersed in water. In addition, the relatively slow action of the hydrolysis process with ambient moisture becomes more rapid and aggressive with high relative humidity or liquid water leading to loss of glycerol-fatty acid linkages. However, in the present experiments hydrolysis is less intense.

The results of these experiments were surprising. The initial steady release of oleic acid from linseed oil was much lower than the linoleic acid from safflower oil, and finally the oleic acid from olive oil was released in significantly less time than the linoleic acid from safflower oil.
for cold pressed linseed oil and the same oil with 0.1 percent by weight copper(II) added. Copper(II) hydroxide was used to introduce copper into the oil because this could be done at near ambient temperatures without altering the oil by excessive heat. Vegetable oils can dissolve some metals. When metal surfaces are coated with oils, metals may be introduced into the oil as the films oxidize, crosslink and dry. In fact, lead kettles have been used in the past to heat linseed oil in preparing the oil for making artists’ paints. The commercial processing of edible oils can introduce enough metal from storage containers to accelerate spoilage or rancidity. Experiments using ICP-MS to measure metal concentrations showed that cold pressed linseed oil when applied to a lead foil reached a concentration of 2.8 percent by weight lead in the resulting gel. Similarly, a cold pressed linseed oil film dried on a clean copper strip contained 0.13 percent copper in the gelled oil at the copper-gel interface and the same oil in bulk with a copper strip immersed reached a level of 1.3 percent dissolved copper after seven days. The dissolved copper shortened the time required for the oil to gel.

The chemistry of oxidation and drying of neat oils is different from that of pigmented oils. Pigments can react with the acids and other compounds produced on oxidation and can inhibit diffusion of oxygen into the film as well as inhibit the diffusion of volatiles out of the film. This will change the amount of weight loss and alter the rate of weight change. Unpigmented oils are, however, a good indicator of the types of processes that do occur but that may be modified either chemically or physically by the presence of pigment particles.

CONCLUSIONS

The data clearly show that there are chemical and physical processes occurring in the oil films for a considerable time after they have gelled. The time of onset of the process of drying (oxidation and gel formation) depends upon the presence of antioxidants that may be removed by either alkali or acid processing but does not affect long term (two-year) behavior. Weight loss depends primarily upon the presence of linolenic acid. The higher the linolenic acid content, the less weight is lost on oxidation. The addition of driers alters the time required for gelling. In the past these driers have been lead, cobalt and manganese compounds intentionally added into pigmented films but lead and copper compounds may be introduced by dissolution from substrate surfaces by the action of the oil itself.

LITERATURE CITED


Associate Editor: Linda L. Thomas

REVIEWERS

Special thanks are extended to the following for reviewing manuscripts: