Effect of Certain Metallic Soaps on the Drying of Raw Linseed Oil[1,2]

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LEAD, manganese, and cobalt and combinations of these metals in the form of their soaps are the commonly used driers for linseed and other drying oils. Iron and copper are two other metals which may be introduced through the heat treatment of a drying oil in kettles made from one of these two metals. In addition, iron has been used as a drier in the manufacture of black varnishes.

In this paper data are presented on the comparative effects of different proportions of these five metals and combinations of them on the drying time of raw linseed oil.

PREPARATION OF METALLIC SOAPS

Fused metallic resinates were selected as a convenient form of the respective metals for introduction into raw linseed oil. They were prepared by customary methods,[3] so that only a brief description of their preparation is necessary.

The resinates were prepared by the fusion of water-white rosin with the acetates of lead, manganese, cobalt, and copper and freshly precipitated ferric hydroxide made from electrolytic iron containing less than 0.01 per cent manganese. The metallic acetates were C. P. reagents.

The lead resinate was light amber in color and contained 6.73 per cent of lead. The manganese resinate was amber colored and contained 2.93 per cent of manganese. The cobalt resinate was ruby colored and contained 3.29 per cent of cobalt. The copper resinate was deep emerald in color and contained 4.16 per cent of copper. The iron resinate was very dark brown and contained 2.76 per cent of iron. All these resinates dissolved to a clear solution in benzene, except iron, which showed traces of sediment.

PREPARATION OF SAMPLES CONTAINING DIFFERENT AMOUNTS OF DRIER

A clear sample of raw linseed oil with an iodine number of 191, which conformed to the requirements of Bureau of Standards (*Circular* 82, 2nd ed., U. S. Government Specification for Linseed Oil), was selected for use in all the drying tests. Stock samples of oil containing definite percentages of metal were prepared by incorporating the necessary amount of the respective metallic resinate in a weighed quantity of oil. The resinate and oil were heated to 150° C., thoroughly shaken, and allowed to cool. In this way thorough mixing was obtained without an appreciable alteration of the oil through heat treatment. Portions of these different stock solutions were diluted with definite amounts of raw linseed oil to give a series of samples with decreasing percentages of metal. These samples were all kept in tightly corked tubes, the air in which had been displaced by carbon dioxide to preclude any preliminary oxidation of the oil.

DETERMINATION OF DRYING TIME OF SAMPLES

The linseed oil samples containing definite percentages of metals were flowed in streaks approximately 2 inches wide on thoroughly cleaned window-glass plates measuring 6 by 8 inches. The excess oil was drained by inclining the plates at an angle of approximately 45 degrees to the vertical for 15 minutes, the bottom edge wiped off, and the plates laid in a horizontal position. The drying tests were made in an evenly heated laboratory, free from combustion or chemical fumes, and lighted by northern exposure. A recording thermometer of the wet and dry bulb type yielded data concerning any fluctuations in temperature or humidity. The average relative humidity during the drying tests was 40 per cent, with a variation from 36 to 43 per cent, with the exception of one 24-hour period when the relative humidity reached 49 per cent. The average day temperature during the drying period was 23.3° C. (74° F.), with a variation from 22.2° to 23.9° C. (72° to 75° F.), while the average night temperature was 20° C. (68° F.), with a variation from 18.9° to 20.5° C. (66° to 69° F.).

The oil films were tested at regular intervals, approximately in the center, 2.5 cm. (1 inch) from the top. The oil was considered to be dry when the finger could be drawn lightly over the surface at an arbitrarily chosen point without marring it. Fairly definite end points could be obtained with the rapid drying oil mixtures; with the slow drying samples the exact length of time for the film to become dry could not be determined with a high degree of accuracy. It should be emphasized that this method for the determination of the drying time involves a considerable personal element, but the data presented are intended chiefly to show the relative catalytic drying effects of the five metals and combinations thereof.

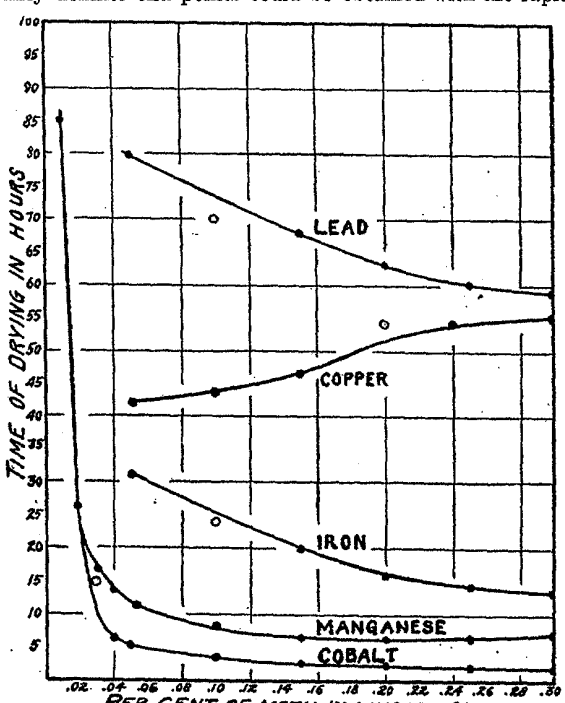

FIG. 1—EFFECTS OF DIFFERENT PERCENTAGES OF LEAD, COPPER, IRON MANGANESE, AND COBALT ON THE DRYING OF LINSEED OIL

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[2] Published by permission of the Director, U. S. Bureau of Standards.

[3] Educational Bureau of the Paint Manufacturers' Association of the United States, *Circular* 120; Seeligmann and Ziecke, "Handbuch der Lack- und Firnisindustrie," p. 701.

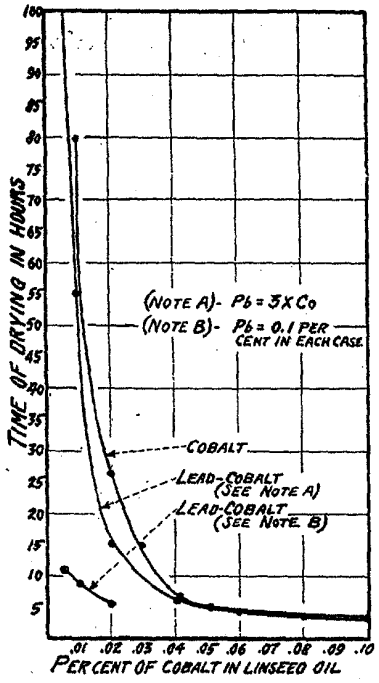

FIG. 2—EFFECT OF LEAD ON DRYING OF SAMPLES OF LINSEED OIL CONTAINING COBALT

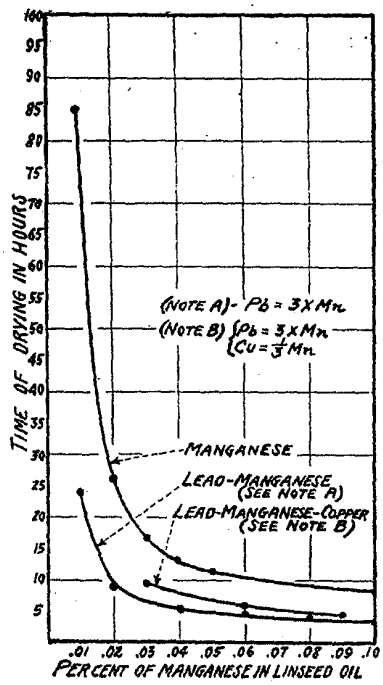

FIG. 3—EFFECT OF LEAD ON DRYING OF SAMPLES OF LINSEED OIL CONTAINING MANGANESE AND EFFECT OF SMALL AMOUNTS OF COPPER ON SAMPLES OF LINSEED OIL CONTAINING LEAD AND MANGANESE

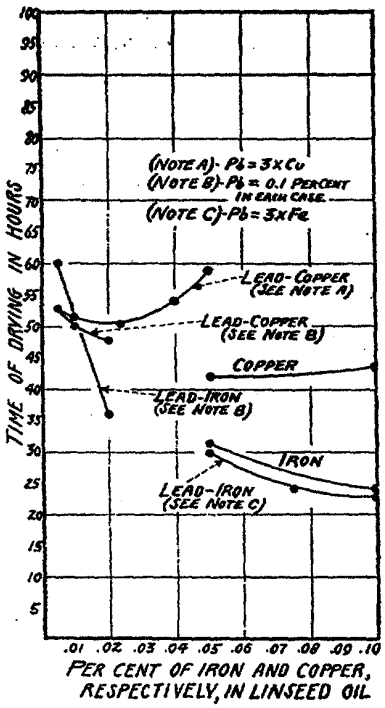

FIG. 4—EFFECT OF LEAD ON DRYING OF SAMPLES OF LINSEED OIL CONTAINING COPPER AND IRON

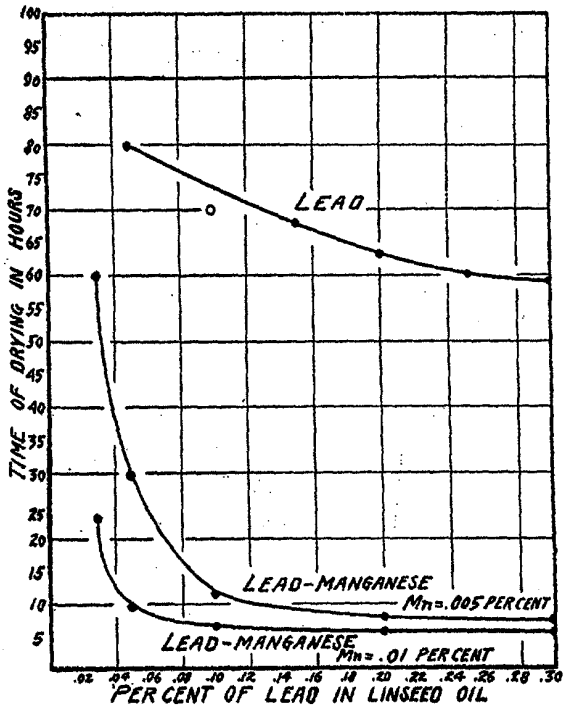

FIG. 5—EFFECT OF A CONSTANT SMALL PERCENTAGE OF MANGANESE ON THE DRYING OF SAMPLES OF LINSEED OIL CONTAINING DIFFERENT AMOUNTS OF LEAD

TABULATION OF RESULTS

All the data on the drying effects of the different metals and their combinations on linseed oil are shown in graphic form in Figs. 1 to 5, inclusive.

DISCUSSION OF DATA

From Fig. 1 it appears that neither copper nor lead resinate alone is an efficient drier for raw linseed oil. Of the five metals studied, copper is the only one that shows any marked increase in drying effectiveness with decrease in concentration. Iron seems to approach manganese and cobalt in effectiveness when used in comparatively high concentrations. The excessively dark color of the iron solutions would be a serious objection to their use. Cobalt appears to be somewhat more effective than manganese in concentrations ranging from 0.3 to 0.03 per cent; below this concentration these metals seem to be nearly equal in their catalytic action, which begins to diminish rapidly at this point with further decrease in concentration. There seems to be practically no advantage in the use of more than 0.05 per cent of either manganese or cobalt to dry linseed oil.

At a concentration of 0.05 per cent of metal, taking cobalt as 100, the relative catalytic effects of the other metals studied would be, roughly, manganese 46, iron 17, copper 13, and lead 6.5.

From Fig. 2 it is seen that if lead is added to samples of linseed oil containing cobalt in the proportion of 3 parts of lead to 1 part of cobalt, there is very little added catalytic effect when the concentration of cobalt is above 0.02 per cent. Lead in the same proportion seems to add effectiveness when cobalt is present in concentrations approximating 0.02 per cent. A greater concentration of lead adds catalytic effect in a marked degree to small concentrations of cobalt. With

0.1 per cent of lead present, an amount of cobalt as small as 0.005 per cent dries linseed oil in less than 12 hours. A more extended study of the effect of different concentrations of lead on small concentrations of cobalt is desirable.

From Fig. 3 it is seen that if lead is added to samples of linseed oil containing manganese in the proportion of 3 parts of lead to 1 part of manganese, there is a marked increase in the catalytic drying effect. A sample of linseed oil containing 0.01 per cent of manganese is changed in drying time from 85 to 24 hours by the addition of 0.03 per cent of lead.

The addition of small amounts of copper to an oil containing lead and manganese appears to have no appreciable effect upon the drying time. This point is of interest because of the possible entrance of copper into linseed oil which has been heat-treated in a copper kettle.

From Fig. 4 it is seen that if lead is added to samples of linseed oil containing iron in the proportion of 3 parts of lead to 1 part of iron, there is no appreciable increase in the catalytic drying action. In no case did samples of linseed oil containing 0.1 per cent of lead and 0.02 , 0.01, and 0.005 per cent of iron, respectively, dry in less than 35 hours. This fact indicates that iron cannot be classed with manganese and cobalt in catalytic drying action.

The addition of lead to samples of linseed oil containing copper in the proportion of 3 parts of lead to 1 part of copper seemed to have a marked retarding effect upon the drying time. In a similar manner, larger amounts of lead with comparatively small amounts of copper did not produce an effective catalytic drying action.

Fig. 5 shows in a marked way the large increase in drying effect obtained by the addition of relatively small percentages of manganese to samples of linseed oil containing different percentages of lead.

There appears to be no advantage in using more than 0.05 per cent of lead in combination with 0.01 per cent of manganese or more than 0.1 per cent of lead in combination with 0.005 per cent of manganese.

In conclusion, it should be emphasized that the data shown in the paper apply to the relative drying effects of certain metals and combinations of these metals when incorporated with raw linseed oil in the form of metallic resinates. The effect of heat treatment during incorporation of the different metals in the manufacture of a true boiled linseed oil has not been considered. Such heat treatment might have a very considerable modifying effect on the catalytic action of the five metals studied.

Silicon in Aluminium-Silicon Alloys[1]

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AN ANALYTICAL chemist who deals with this class of alloys is sometimes at a loss when his results do not agree, and although all probable variables have been kept practically constant, he frequently desires considerably more accuracy. The general rule in such a case is to attribute the discrepancies to the lack of uniformity of the sample. Though the lack of uniformity in the aluminium-silicon series is sometimes very pronounced, a wrong assumption seems to be responsible for devising the methods now in general vogue, and which are therefore inherently inaccurate.

In textbooks of inorganic chemistry and, to the author's knowledge, in all treatises on analysis, it is generally stated that so-called "graphitic" silicon obtained in the course of analysis cannot be oxidized to silicon dioxide by ignition and remain unaffected when treated with a mixture of hydrochloric, nitric, and sulfuric acids generally used for decomposition of the sample. During some investigations on the microstructure of aluminium-silicon alloys undertaken in this laboratory, certain lack of coördination between the structure of metal as seen under a microscope and the results of analytical determinations led to a closer study of the properties of silicon, especially its graphitic variety, and resulted in two statements, the accuracy of which was proved:

1—Graphitic silicon is oxidized to silicic acid when heated with a mixture of hydrochloric, nitric, and sulfuric acids.

2—Graphitic silicon rapidly oxidizes when subjected to the temperature and for the length of time necessary for dehydration of silica. The amount of oxidation is closely related to the temperature and time of ignition.

In other words, the amount of graphitic silicon in a certain alloy is not a definite quantity, but a function of the composition and amount of acid mixture used for solution of the sample, temperature, and time of ignition. With a considerable degree of certainty the theory may be advanced that in an alloy silicon is present in a state which, after proper treatment, will yield 100 per cent of its graphitic variety. The fact that some silicon dioxide is always present finds its explanation in the oxidizing power of the factors entering a routine analysis, which is sufficiently intense to convert particles of silicon that are very minutely divided—as, for example, in solid solution—into silicic acid during the comparatively short time used in an ordinary analytical determination.

If, being powerless to increase materially the concentration of the acids employed, we intensify other variables affecting oxidization, such as time and temperature of ignition, we shall observe in a given sample a gradual transformation of the ratio of silica to graphitic silicon. The percentage of silica will be continuously increasing and, under proper conditions, no graphitic silicon will be present. The intensity of the necessary conditions is in close relation to the silicon content of the sample, comparatively little depending on the heat treatment to which the alloy is subjected.

It is quite impossible to consider the amount of silicon in a given sample present in the graphitic state as an absolute value. If no standardization of analytical procedure is made, the results obtained will be in inadmissible discord. If all details are carefully standardized and closely adhered to, one may be sure of the amount of graphitic silicon, but for a different set of conditions, a different value will result.

Microscopic examinations and study of cooling curves support the theory that silicon is present in alloys in one modification, graphitic silicon, which as such, instead of being an ingredient the presence of which may indicate certain properties of the alloy, becomes just an undesirable complication in analytical work.

A method was devised which eliminates from consideration graphitic silicon and, without being long or elaborate, gives dependable data for routine determinations:

[1] Received March 3, 1924.