Place a 0.5-gram sample of well-mixed borings in a 50-cc. iron crucible and add 2 grams of solid sodium hydroxide. Cover with a watch glass and moisten with 1 cc. of water. When the violent action ceases, add 9 cc. of water, place on a hot plate, and heat for 30 minutes. At the beginning the liquid boils rapidly, but later, when most of the water has been expelled, no ebullition is observed. Without cooling, transfer the contents of the crucible into a porcelain evaporating dish. Rinse the crucible carefully with water, 35 cc. of acid mixture, and then with water again. Collect the washings in the evaporating dish into which the melt was transferred. Evaporate to dryness and fume strongly for 5 minutes. Cool, take up with 50 cc. of sulfuric acid (1 : 10) and boil until the solution is complete. Filter on ashless filter paper. Wash at least six times with water. Ignite in a platinum crucible and weigh. Add a few drops of sulfuric acid, about 20 drops of hydrofluoric acid, evaporate carefully on edge of a hot plate, and ignite. The difference in weight will give the amount of silicon present expressed as SiO_2.

To prepare acid mixture, mix in the order given, 300 cc. sulfuric acid (specific gravity 1.84), 300 cc. water, 300 cc. hydrochloric acid (specific gravity 1.19), and 100 cc. nitric acid (specific gravity 1.42).

Blanks for deduction should be run on reagents used.

Effect of Iron Oxide Pigments on Rate of Oxidation of Linseed Oils[1]

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The red iron oxide pigments tend first to retard and then to accelerate the oxidation of linseed oil in paint films. Partially hydrated iron oxide is more active than is the anhydrous oxide, while the presence of calcium carbonate in the pigment renders it less active in accelerating the oxidation. Black iron oxide is a relatively inert pigment, although it retards slightly the oxidation of the oil.

THE effect of certain paint pigments on the rate of drying of linseed oil has been studied by Rhodes and Van Wirt.[2] This investigation, however, was confined to the study of the effects of various white paint pigments, and no attention was paid to the iron oxides or to any of the other colored pigments. In view of the great importance and the extensive use of the iron oxide pigments, it was thought advisable to make the study of the effect of these pigments the subject of a separate investigation. The present article describes the results obtained with various typical iron oxide reds and with black oxide. The work on the yellow and brown iron pigments is as yet incomplete.

MATERIALS

The materials used in this work were pure, refined linseed oil from North American seed, lead linoleate paste drier, and representative iron oxide pigments obtained from various manufacturers. The linseed oil showed the following analysis:

Specific gravity at 15.5° C.	0.934
Refractive index at 25° C.	1.4803
Acid number	0.473
Saponification number	193.3
Iodine number	173.

The analyses of the various pigments employed are shown in Table I.

[1] Received June 17, 1924.

[2] THIS JOURNAL, 15, 1135 (1923).

PROCEDURE

The apparatus used and the procedure followed in determining the rate of oxidation of the oil in the presence of the pigments were essentially similar to those described by Rhodes and Van Wirt.[2] Paints were prepared by grinding together two parts by weight of the pigment to be studied and three parts by weight of the vehicle. In each case the vehicle was prepared by dissolving in the linseed oil a sufficient quantity of lead linoleate paste (17 per cent lead) to contain an amount of lead equivalent to 0.2 per cent by weight of the oil. The paints were allowed to stand in sealed containers for at least 2 weeks before use. Weighed samples were then spread on cloth and exposed to an atmosphere of pure oxygen at 30° C., and the rate of absorption of oxygen and the rate of evolution of volatile matter were measured. The rate of oxidation of the vehicle alone (linseed oil with 0.2 per cent lead) was determined in a similar manner. In each case at least two determinations were made with each paint. The individual determinations gave results which agree with each other within the limits of experimental error.

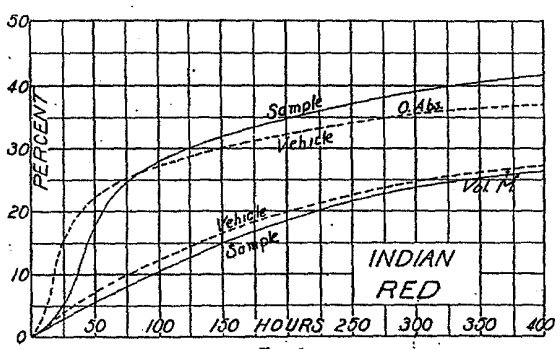

FIG. 1

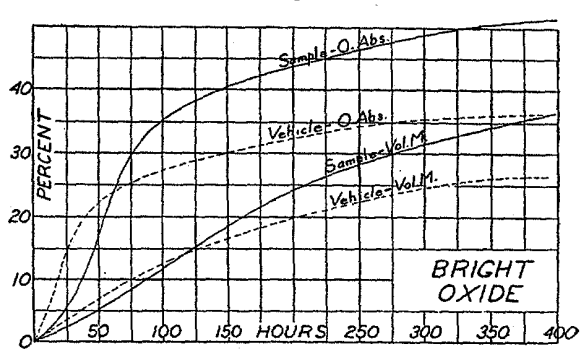

FIG. 2

RESULTS

The results are shown graphically by the accompanying curves, in which the amounts of oxygen absorbed and the amounts of volatile matter evolved (each expressed in terms of percentage by weight of the oil in the paint) are plotted

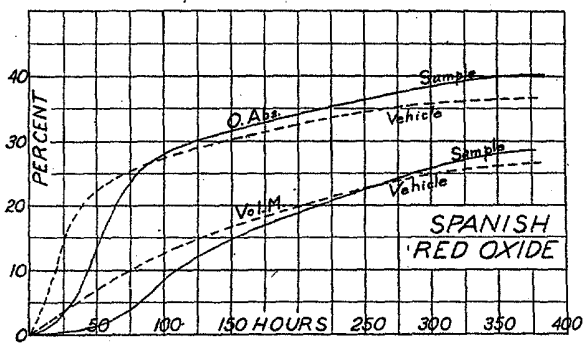

FIG. 3

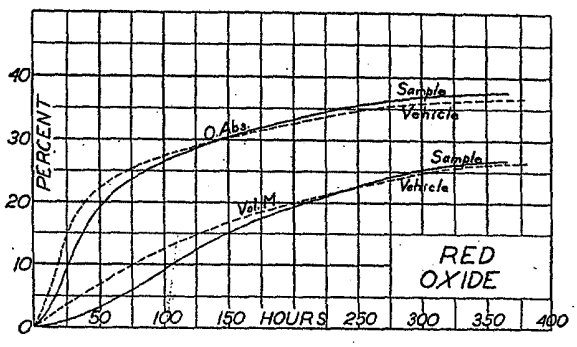

FIG. 4

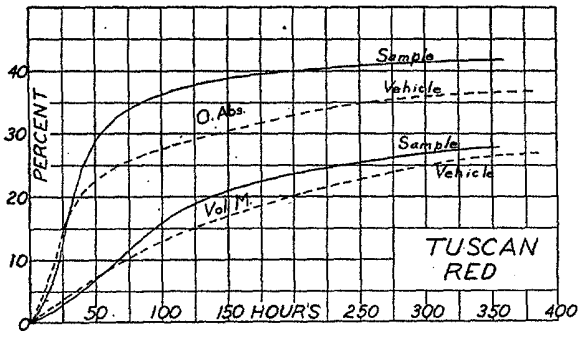

FIG. 5

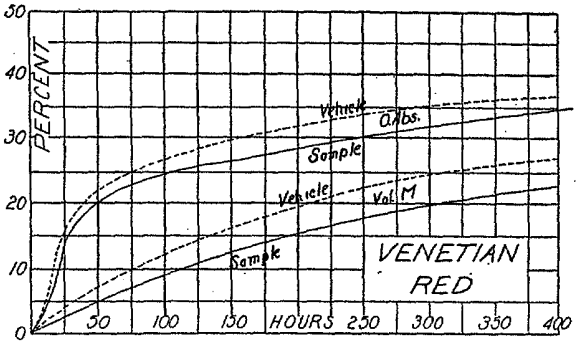

FIG. 6

against the lengths of time of exposure. For each pigment there is plotted only one curve, depicting the average results of the two or more check determinations. On each diagram the graphs for the rate of absorption of oxygen by the vehicle alone and for the rate of evolution of volatile matter from the vehicle alone are shown for purposes of comparison. These graphs are drawn as dotted lines.

INDIAN RED (Fig. 1)—This pigment first retards and then increases the rate of absorption of oxygen by the vehicle. The initial retardation does not seem to be due to the mere physical effect of the pigment in increasing the thickness of the film and preventing rapid diffusion of oxygen into the mass, but to a specific effect of the iron oxide in accentuating the initial period of induction of the oxidation reaction. One hypothesis which may explain this effect is that the finely divided ferric oxide absorbs some of the lead drier and thereby lowers the concentration of this catalyst in the oil. The subsequent acceleration of the oxidation is probably due to the reaction of the iron oxide with some component of the vehicle or with some oxidation product of the oil, with the resulting formation of a salt or soap of iron which acts as a drier. In this respect Indian red appears to behave somewhat like Carter white lead.[2]

If compounds of iron which act as driers in the oxidation of linseed oil were formed by the direct action of the ferric oxide on the oil itself, we should expect these compounds to be produced during the 2 weeks' period of aging to which the paints were subjected before being exposed. That such was not the case is apparent from the form of the oxidation curve; the driers are formed *after* the oxidation starts. Apparently, therefore, the iron oxide reacts with certain acidic oxidation products formed during the drying of the oil. Of course it is possible that in a highly acid, unrefined oil iron driers may be formed in the paint before it is exposed to air.

BRIGHT OXIDE (Fig. 2)—In general form this oxidation curve resembles that obtained with Indian red, but the effect of the pigment in promoting the oxidation of the oil is much more pronounced than in the case of the Indian red. The "bright oxide" also more markedly increases the rate of evolution of volatile matter. The differences in the amounts of iron oxide or in the amounts of impurities in the two reds are, at first glance, hardly sufficient to explain the difference in their effects on the oxidation. It will be observed, however, that the "bright oxide" contains a relatively large amount of combined water, while the Indian red contains but very little moisture. Apparently, the partially hydrated ferric oxide of the "bright oxide" is much more reactive and forms iron driers much more readily than does the more nearly anhydrous ferric oxide of the Indian red.

TABLE I

PIGMENT	Fe_2O_3 Per cent	SiO_2 Per cent	$BaSO_4$ Per cent	Al_2O_3 Per cent	MnO Per cent	$CaCO_3$ Per cent	$MgCO_3$ Per cent	$CaSO_4$ Per cent	Free H_2O[a] Per cent	Combined H_2O[b] Per cent
Indian red	98.77	0.83	..	..	0.15	..	..	..	0.46	0.10
Bright oxide	93.30	1.10	..	..	0.75	..	..	0.52	0.77	3.84
Spanish red oxide	87.92	6.93	..	1.55	0.21	1.01	..	..	0.39	1.38
Red oxide	86.52	6.57	..	0.70	0.31	5.88	..	..	0.50	0.31
Tuscan red[c]	14.75	0.13	6.55	3.27	0.11	..	..	6.46	2.85	3.65
Venetian red	9.24	1.22	..	0.22	0.43	85.93	1.01	..	0.79	1.27
Black oxide[d]	96.96	1.10	..	..	0.75	..	..	0.52	0.77	3.84

[a] Loss on drying 3 hours at 105° C.
[b] Includes organic matter.
[c] Contains a considerable amount of a red organic coloring matter.
[d] Calculated as Fe_3O_4.

SPANISH RED OXIDE (Fig. 3)—This gives results quite similar to those obtained with Indian red, although the initial inhibitory effect is somewhat more pronounced. The Span-

ish oxide contains a considerable amount of combined water and might be expected, from analogy with the "bright oxide," to show a much more marked drying action than does the Indian red. The Spanish oxide, however, contains a small amount of calcium carbonate, while the "bright oxide" is free from such basic impurity. It is reasonable to suppose that the calcium carbonate would tend to neutralize some, at least, of the acidic products of the oxidation of the oil and would thus decrease or prevent the formation of the iron drier.

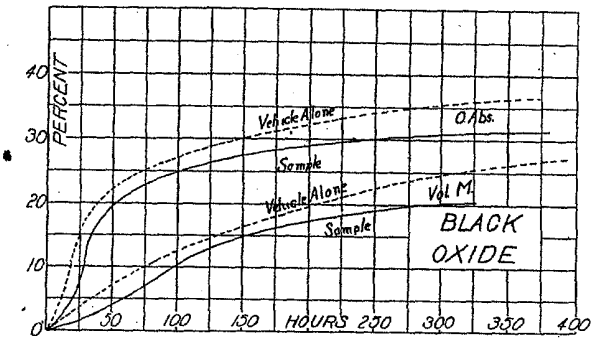

FIG. 7

RED OXIDE (Fig. 4)—This effect of calcium carbonate in inhibiting the drying action of the iron oxide is exhibited even more markedly in the case of the red oxide. This pigment, which contains 4.88 per cent of calcium carbonate, gives a paint the oxidation curve of which is very nearly identical with the curve for the oxidation of the vehicle alone.

TUSCAN RED (Fig. 5)—With the Tuscan red the effect of the pigment in decreasing the initial rate of oxidation of the oil is very slight. This might be expected, for this pigment contains only a relatively small amount of ferric oxide. The ferric oxide present, however, is in a rather highly hydrated and very active form, so that the iron driers are formed readily and the pigment shows a very pronounced accelerating effect shortly after the beginning of the period of exposure.

VENETIAN RED (Fig. 6)—This pigment gives results that are quite consistent with those obtained with the preceding pigments. Because of the low percentage of ferric oxide in the Venetian red the initial inhibiting effect on the oxidation is very slight, while the large amount of calcium carbonate in the pigment prevents the formation of any iron drier during the drying of the oil.

BLACK IRON OXIDE (Fig. 7)—This decreases the rate of oxidation of the oil throughout the whole period of drying. The initial retardation, however, is not nearly so pronounced as in the case of Indian red. The black oxide appears neither to adsorb the lead drier to a marked extent nor to react with the oil to form iron driers. To a certain extent the black oxide resembles lithopone in its effect on the oxidation of linseed oil.

CONCLUSIONS

The results obtained in this investigation justify the following conclusions:

1—The iron oxide reds (including Tuscan red and Venetian red) tend first to inhibit and then to accelerate the oxidation of linseed oil containing lead drier. The initial inhibiting action may be due to the adsorption of the lead drier by the pigment, although we have no direct experimental evidence to support this hypothesis. The subsequent accelerating action is due, presumably, to the formation of small amounts of ferric compounds which are soluble in the oil and which act as driers.

2—The formation of the iron driers takes place during the drying of the oil and is due to the interaction of the pigment with acidic products formed during this oxidation.

3—Iron oxide reds that contain partially hydrated ferric oxide are much more active in accelerating the oxidation of the oil than are the more nearly anhydrous oxides.

4—The presence of basic substances—as, for example, calcium carbonate—tends to prevent the formation of iron driers during the drying of paints containing iron reds, and thus prevents the pigments from exhibiting their normal effect in accelerating the reaction.

5—Black oxide shows only a slight effect in inhibiting the initial oxidation of the oil, and displays no tendency to react with the oil to form iron driers.

Things Not Known about Rubber

The souvenir number of the *India Rubber Journal*, which commemorates its fortieth anniversary and which was issued August 2, 1924, contains the following among "More Things Not Known about Rubber."

What happens when raw rubber "freezes?"

Why is frozen rubber opaque and thawed rubber transparent?

Why do basic substances have an accelerating and acidic substances a retarding effect in vulcanization? (A simple rubber-sulfur mixture is here in mind.)

Can rubber particles in latex be subdivided—i. e., further dispersed?

Can vulcanized rubber, or crude rubber, or both, be stabilized to such an extent that deterioration or "perishing" shall be no greater than in the case with metals, such as gold or aluminium, or with organic substances, such as horn, leather, wood, and the like?

Why is rubber that is kept in use—i. e., mechanically worked—less liable to deterioration than rubber that remains quiescent?

Does rubber possess coarse—i. e., nonmolecular—structure, and, if so, how does this structure bear on the mechanical properties?

Or are the properties of rubber explainable solely by virtue of its molecular constitution and the grouping of the molecules to form definite aggregates?

Why do finely divided, insoluble compounding ingredients reinforce rubber?

Why have the two forms of finely divided carbon—viz., lamp black and gas black—such widely different effects on rubber in which they are compounded?

To what extent does flocculation really occur among the particles of the compounding ingredients in rubber after vulcanization?

Why does synthetic rubber age more rapidly than natural rubber?

What are the effects of (*a*) air, (*b*) light, and (*c*) temperature in the natural aging of vulcanized rubber?

Why does vulcanized rubber age less rapidly in moist air than in very dry air?

How many other factors affect the aging qualities of manufactured rubber?

Why do the soluble serum substances of latex offer such great resistance to removal in washing latex rubber?

What alteration in the molecular or colloidal structure of rubber occurs in the softening of rubber by milling or by heating?

To what extent is the effect of softening rubber by heat comparable with that of softening by milling?

To what extent is the action of atmospheric oxygen an important factor in the softening of rubber by milling?

Are the great differences observable between the resistance of milling of various natural rubbers caused by differences in the rubber hydrocarbon or by differences in the noncaoutchouc—e. g., pro tem—substances present?

What is the exact nature of the physical alteration in rubber on vulcanization?

When will it be possible to produce "raw" rubber from vulcanized scrap by total removal of the free and uncombined sulfur and the fillers?

Exactly what happens when rubber swells or "dissolves" in a liquid?