# Effect of Zinc Oxide Pigments upon Rate of Oxidation of Linseed Oil[1]

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IN THEIR preliminary work on the effect of various pigments on the oxidation of linseed oil, Rhodes and Van Wirt[2] found that under certain conditions zinc oxide causes an oxidizing film of linseed oil to set or harden at an early stage in the oxidation. They did not, however, determine the cause of this hardening or the extent to which it depends upon the exact composition of the pigment. The work described in the present article was undertaken for the purpose of investigating more closely the relation existing between the exact composition of a zinc oxide pigment and the effect of that pigment upon the drying of linseed oil.

**Pure zinc oxide has no effect on the rate of oxidation of linseed oil. Zinc oxide containing lead as an impurity may increase the rate of oxidation because of the formation of lead driers by interaction between the oil and the pigment. The presence of soluble compounds of zinc causes the drying oil to coagulate at an earlier stage in the oxidation and to form a harder and less permeable film. The action of soluble compounds of zinc as coagulants or hardeners for linoxyn explains many of the observed phenomena in connection with the use of zinc oxide pigments and zinc driers.**

## Materials

The linseed oil used in this work was pure refined oil from North American seed. It showed the following analysis:

| | |
|---|---|
| Specific gravity at 15.5° C. | 0.938 |
| Refractive index at 25° C. | 1.4801 |
| Acid number | 0.496 |
| Saponification number | 193.5 |
| Iodine number | 173.7 |

The analyses of the pigments used are shown by Table I.

**Table I—Analyses of Pigments**
(Figures in per cent)

| PIGMENT | $H_2O$ | $SiO_2$ | $SO_3$ | Pb | $ZnSO_4$ |
|---|---|---|---|---|---|
| U. S. P. Zinc Oxide | 0.10 | 0.37 | 0.00 | 0.02 | 0.05 |
| Kadox Black Label | 0.10 | 0.50 | 0.00 | 0.23 | 0.15 |
| Red Seal | 0.03 | 0.50 | 0.01 | 0.22 | 0.11 |
| White Seal | 0.07 | 0.53 | 0.00 | 0.30 | 0.14 |
| Standard American | 0.07 | 0.24 | 0.03 | 1.95 | 0.41 |

## Procedure

The procedure used was essentially similar to that described by Rhodes and Van Wirt.[2] Paints prepared from zinc oxide and linseed oil were 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. Each paint was made up from two parts by weight of pigment and three parts of linseed oil in which had been dissolved sufficient lead linoleate to contain an amount of lead equivalent to 0.2 per cent by weight of the oil. All paints were aged by being allowed to stand for 2 weeks in a sealed container before being tested. With each paint there were made two or more parallel determinations, giving results which agreed to within the limits of experimental error.

## 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 against the lengths of time of exposure. A single curve is shown to represent the average results of the two or more check determinations made with each paint.

U. S. P. ZINC OXIDE (FIGURE 1)—This pure zinc oxide has very little effect on the rate of oxidation of the oil. The slight retardation of the initial rate of oxidation may be due to a slight adsorption of the lead drier or simply to the mechanical effect of the pigment in retarding the diffusion of oxygen into the interior of the film.

KADOX BLACK LABEL ZINC OXIDE (FIGURE 2)—Paints made with this pigment harden somewhat more rapidly than do those made with the purer U. S. P. zinc oxide, so that the diffusion of oxygen into the film of partly oxidized oil takes place more slowly and the final oxidation of the oil is retarded. Red Seal and White Seal zinc whites gave results which were so nearly identical with those obtained with the Kadox Black Label oxide that a single curve may be drawn to represent all three sets of results. The most significant differences in composition between these three pigments and the U. S. P. material are in the amounts of lead and of zinc sulfate which are present. Since the larger amount of lead in the Kadox oxide should tend to increase rather than to decrease the final rate of drying, it seems reasonable to assume that the soluble salts of zinc are responsible for the more rapid hardening of the oil and the decrease in the final rate of oxidation.

STANDARD AMERICAN ZINC WHITE (FIGURE 3)—This pigment at first slightly retards the oxidation but later accelerates it. The initial retardation may be due to the partial adsorption of the lead drier by the pigment. The final acceleration is probably caused by the interaction of the compounds of lead in the pigment with the acidic products of the oxidation of the oil, with the resulting formation of lead driers. It will be observed that with the U. S. P. zinc oxide, which is practically free from lead, no such acceleration of the final drying takes place.

EFFECT of SOLUBLE COMPOUNDS OF ZINC (FIGURE 3)—If the presence of very small amounts of soluble salts of zinc does cause the more rapid and more marked hardening of the drying oil, it should be possible to cause this hardening to take place to a greater extent and at an earlier stage in the oxidation by adding soluble compounds of zinc to the paint. Paints were prepared from Standard American zinc white to which had been added 5 per cent by weight of dehydrated zinc sulfate, and from Standard American zinc white to which had been added 5 per cent by weight of zinc linoleate (obtained by adding a solution of zinc sulfate to a neutral solution of sodium linoleate and drying the resulting precipitate). The paint containing the zinc sulfate showed sudden and marked hardening after about 50 hours' exposure. The hardened film continued to oxidize very slowly, so that the total amount of oxygen absorbed after 400 hours' ex-

[1] Received June 16, 1925.
[2] THIS JOURNAL, 15, 1135 (1923).

posure was only 32 per cent instead of 43 per cent, as in the case of the paint made with the pigment to which no zinc sulfate had been added. The paint containing zinc linoleate hardened after about 25 hours' exposure, but the hardened film was somewhat more permeable to oxygen and continued

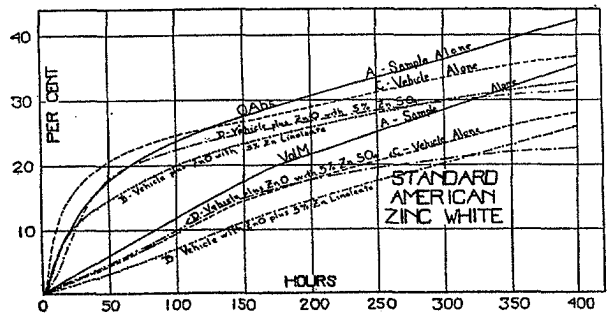

Figure 1

to oxidize more rapidly than did the film from the paint containing zinc sulfate, so that the total amount of oxygen taken up in 400 hours was about the same in the two cases.

### Discussion

Pure zinc oxide, free from lead and from soluble compounds of zinc, has no effect upon the rate of oxidation of well-refined linseed oil and does not affect the hardness or other characteristics of the linoxyn film formed during at least the first 400 hours of drying.

The presence of compounds of lead in the zinc oxide tends to increase the rate of oxidation of the oil. This effect is probably due to the formation of lead driers by the interaction of the lead compounds in the pigment and the acidic products of the interaction of the oil. Very probably the extent to which this drying effect of the lead compounds appears depends, not only on the amount of the lead in the pigment, but also upon the form in which this lead is present.

The presence of soluble compounds of zinc tends to cause the oil to gelatinize or solidify at an early stage in the oxidation and to form a harder and more dense film. Among the soluble compounds of zinc that may find their way into a paint are zinc sulfate, which may be introduced as an impurity in the zinc oxide pigment, and zinc linoleate, which may be formed by the interaction of the zinc oxide with a linseed oil of high acidity. It is interesting to note that lithopone, which may also contain small amounts of soluble compounds of zinc, also acts as a hardener for linoxyn and tends to inhibit the final oxidation of the film.[2]

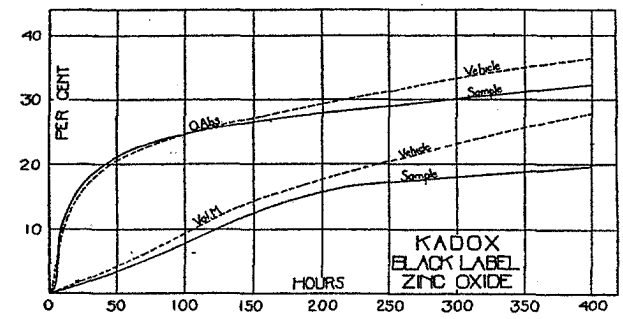

Figure 2

This action of soluble compounds of zinc as coagulants or hardeners for linseed oil explains many of the phenomena that have been observed in connection with the use of zinc oxide pigments. It is commonly recognized that "zinc oxide paints are harder and less elastic than white lead paints,"[3] and that "the addition of zinc oxide to a white lead paint renders it sufficiently hard to resist some of the peculiarly inherent forms of decay and discoloration.[4] Since other very fine pigments do not show the same effect, this hardening cannot be due to the merely physical action of the finely divided zinc white in decreasing the voids in the film, but must be caused by some change in the hardness of the oxidized vehicle. The zinc oxide causes the linoxyn film to harden and thus gives a film which is not only firmer but less permeable to oxygen and therefore more resistant to the slow "after oxidation" which is responsible for the gradual disintegration and ultimate destruction of the paint. If the paint contains too much zinc in soluble form, however, the hardening effect may become so pronounced that the dry film fails because of brittleness. Excessive amounts of soluble zinc may also tend to gelatinize or coagulate the liquid paint and may therefore cause "stiffening," "livering," or "granulation." Such excessive amounts of soluble zinc may be introduced by the use of a zinc white, which contains zinc sulfate,[5] or by grinding zinc oxide in an oil of high acid value.[3,6]

A number of investigators have found that the addition of soluble compounds of zinc to linseed oil decreases the time required for the film of oil to become dry to the touch, and have therefore classified zinc, along with lead, manganese, cobalt, and iron, as a drier for linseed oil. Many of the

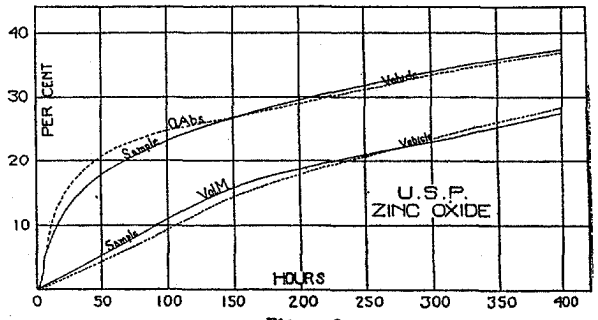

Figure 3

special patent driers contain zinc sulfate as an essential ingredient. The writers' experimental work has shown that zinc is not, properly speaking, a *drier*, but is a *hardener* for linseed oil. Compounds of zinc do not catalyze the oxidation of the oil, but they do cause the oil to solidify at an earlier stage in the oxidation. Since, as is well known, paints made with lampblack or carbon black sometimes tend to remain sticky for a long time, it would appear that the addition of zinc sulfate or zinc linoleate to such paints would be of considerable advantage.[7]

[3] Sabin, "Technology of Paint and Varnish," 1917, p. 184.
[4] Gardner, "Paint Researches and Their Practical Applications," 1917, p. 27.
[5] Holley, "Lead and Zinc Pigments," 1909, p. 178.
[6] Morrell and de Waele, "Rubber, Resins, Paints, and Varnishes," 1920, p. 118.
[7] Toch, "Chemistry and Technology of Paints," 1916, p. 45.

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Salvarsan, neosalvarsan, salvarsan compounds, acetanilide, acetylosalicylic acid, diethylbarbituric acid, caffeine, dimethylaminoantipyrine, oxydimethylquinizinepyrazoline, iodoform, potassium sulfoguaiacolicum, sodium diethylbarbituric acid, phenylquinolinecarboxylic acid, phenyldimethylpyrazoline; and quinine, cocaine, codeine, guaiacol, morphine, novacaine, and theobromine and their salts.