Oxidation of Unbodied Linseed Oil

Antioxidant Influence of Phenol-Formaldehyde Resins on Unbodied Linseed Oil in the Presence of Driers

C. C. VERNON AND W. W. RINNE
University of Louisville, Louisville, Ky.

THE phenomenon known as drying of certain unsaturated polymerizable oils has been long known. Many factors govern this drying, and many substances when mixed with oil accelerate or retard it. Many theories have been proposed in an effort to explain this behavior.

It is generally recognized that oxidation and polymerization are the principal factors involved in the process. The oxidation is believed to be confined to addition of oxygen to unsaturated carbon atoms of those acids whose esters comprise the major part of a drying oil. The gain in weight following such addition of oxygen provides an approximate criterion of the rate of oxidation, despite the fact that volatile products are evolved during the drying process, especially at the end of it.

Moureu and Dufraisse (*5*) proposed a theory relative to inhibition of autoxidation processes in general, which has been helpful in planning this study and which has indicated some of the procedures followed. This theory holds that antioxidants are themselves oxidizable substances with the antioxygenic property localized in the oxidizable part of the molecule. Prominent among the antioxidants of Moureu and Dufraisse are phenols, which are used in the production of many synthetic resins. Several investigators (*4, 9, 10*) have shown that phenolic compounds inhibit the oxidation of linseed oil during the induction period. Other investigators (*1, 8*) have inferred the presence of free phenols in synthetic resins. Careful tests of the samples used in this investigation, using diazotized *p*-nitroaniline as well as ferric chloride, showed the absence of any considerable amounts of unreacted simple phenol left there from the manufacturing process. In one instance a somewhat complex phenol was detected and removed.

Synthetic resins have been used in the manufacture of varnishes for some time. Such varnishes have dried satisfactorily, although the effect of the resins on such drying has varied. This behavior must not be confused with the results reported for this study. The oil used in the manufacture of these varnishes was heat-bodied to begin with, became heat-bodied during the process, or else was tung oil which has a conjugated system of double bonds particularly susceptible to polymerization. This study was limited to unbodied oil, and the results attained should not be compared to those where bodied oils were used.

This investigation, using commercial materials, showed that the six phenolic resins tested increased the induction period in the oxygen absorption of unbodied linseed oil in the presence of driers, in direct proportion to the amount of resin present. The behavior of the oil after the induction period was apparently unaffected, since it eventually dried completely. Mixtures of synthetic resins with ester gum had the same effect as the pure resins, but to a less degree since the proportion of resin was less. Treatment of two of the three resins that showed the most marked antioxidant effect with an oxidizing agent resulted in a diminution of this effect.

Method

After a study of the limitations of such methods as ultimate analysis, volumetric measurement of oxygen absorption, and blowing with conditioned air, the simple gain-in-weight method was chosen.

This method gave only the apparent rate of oxygen absorption, but in a study such as this one where conclusions were to be drawn from a comparison of data collected under identical experimental conditions, it was considered adequate. It had the further advantage of rapidity, making possible many readings in the time available.

The resin-oil solutions were prepared in concentrations calculated as per cent by weight. Each constituent was weighed to 0.5 mg. on an analytical balance; for each gram of oil in the solutions, 0.0427 gram of naphthenate drier was included, the metal content of which is given in the section headed "Materials." The mixture was heated to 150° C. for 5 minutes to ensure complete dispersion, sealed in vials, and stored in a dark cabinet 2 days before use. The mixture so prepared was then spread on slightly etched, tared glass plates so that an area of approximately 95 sq. cm. was exposed. These plates were weighed immediately and at timed intervals thereafter; the intervals were governed by the rapidity of drying. The initial weights of the films so prepared varied from 0.1000 to 0.2580 gram, depending on the thickness of the film which, in turn, was governed by the viscosity of the original solution. No attempt was made to govern the thickness of the films, except to keep it within the limits prescribed by Wise and Duncan (*11*) who showed that reasonable variation did not appreciably affect the rate of oxidation. The present writers' experience in securing checks with films of the same resin mixture but varying in weight, and therefore thickness, confirmed the finding of these investigators.

Since temperature (*6, 10*), humidity (*7*), and light (*3*) all influence the drying of oils, it was necessary to carry out the experiments under conditions such that these factors were as nearly constant as possible. During the day the films were exposed to diffused light, and the temperature variation for the test periods was held within 2° C. limits. The humidity was much more difficult to control, but it was found that data collected when the humidity varied from 50 to 60

agreed within the limits of experimental error. Most of the data were collected at an average of 55.

Weighings were made over a period of 180 hours, the intervals being longer after 60 hours. The most satisfactory agreements were secured during the first 15 hours, after which time uncontrollable factors caused some variation.

Materials

The resins investigated met the usual industrial specifications and contained the amount of phenolic resin indicated in the following table. The diluent for those resins specified as less than 100 per cent phenolic was ester gum. The numbers given provide the key for reference in the discussion:

Resin No.	Approx. Phenolic Resin Content, %	Test for Free Phenol	Resin No.	Approx. Phenolic Resin Content, %	Test for Free Phenol
1	100	–	4	45	+
2	100	–	5	20	–
3	100	–	6	14	–

The alkali-refined linseed oil used had the following values:

Iodine No., Wijs method	185.3
Acid No.	0.65
Saponification value	193.20
Specific gravity	0.931

The metal content of the naphthenate drier used was 0.30 per cent cobalt, 0.30 per cent manganese, and 4.60 per cent lead; the specific gravity of the drier was 0.855.

Consideration of Curves

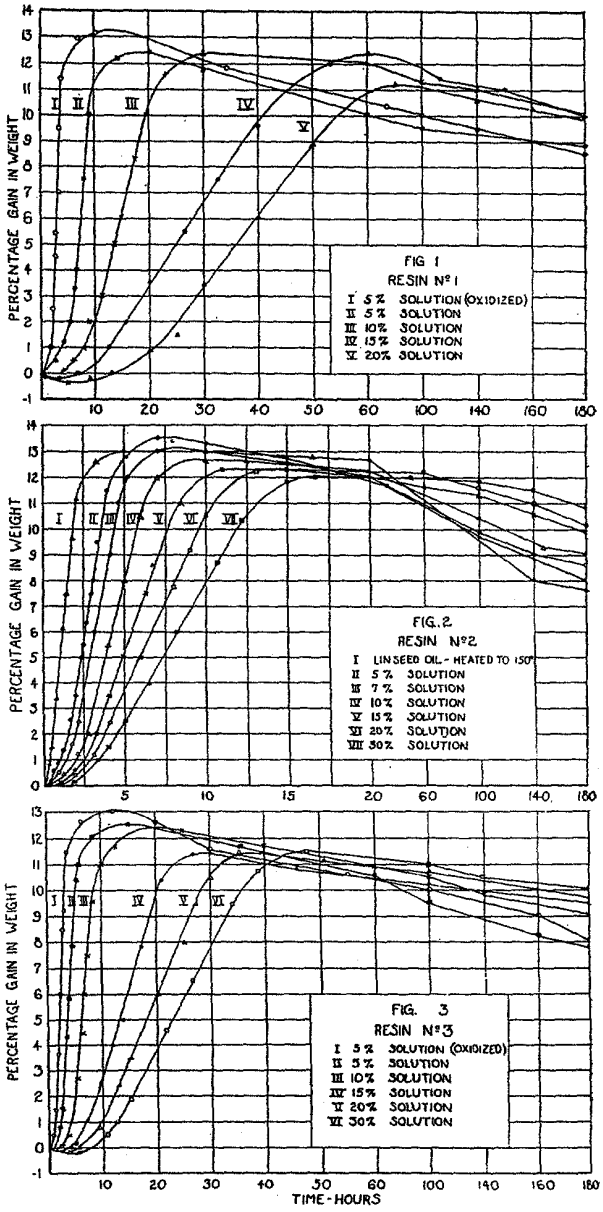
The curves presented represent the percentage gain in weight of the oil in the resin-oil mixtures, not that of the entire mixture. It was shown in preliminary studies that thin films of the resin, spread from ether suspensions or solutions, did not gain in weight when exposed to air under the experimental conditions which prevailed during this study. The amount of oil present in any given sample was easily determined from the original weight of the film and the percentage composition of the solution. The "raw" data were all recalculated by the use of an appropriate conversion factor so that the new data showed the percentage gain in weight of the oil.

The conclusions were drawn by comparing the curves for the resin-oil mixtures with curves for linseed oil without resin; both curves were from data collected under identical experimental conditions. This method had the advantage that the inherent defects of the gain-in-weight method were eliminated.

Each of these curves represents data collected in several runs under similar conditions and agreeing within the usual experimental limits. In addition to curves representing the resin-oil mixtures is the curve showing the behavior of linseed oil (Figure 2, I) and a curve (Figure 5, I) showing the behavior of ester gum, the diluent for resins 4, 5, and 6. The data for these curves were collected under the experimental conditions prevailing during this study and the curves have been included for comparison with the resin-oil curves.

The curves for the 100 per cent phenolic resins (Figures 1, 2, and 3) show that each of these had antioxidant influence, in direct proportion to the amount of resin present. This effect was confined for the most part to the induction period.

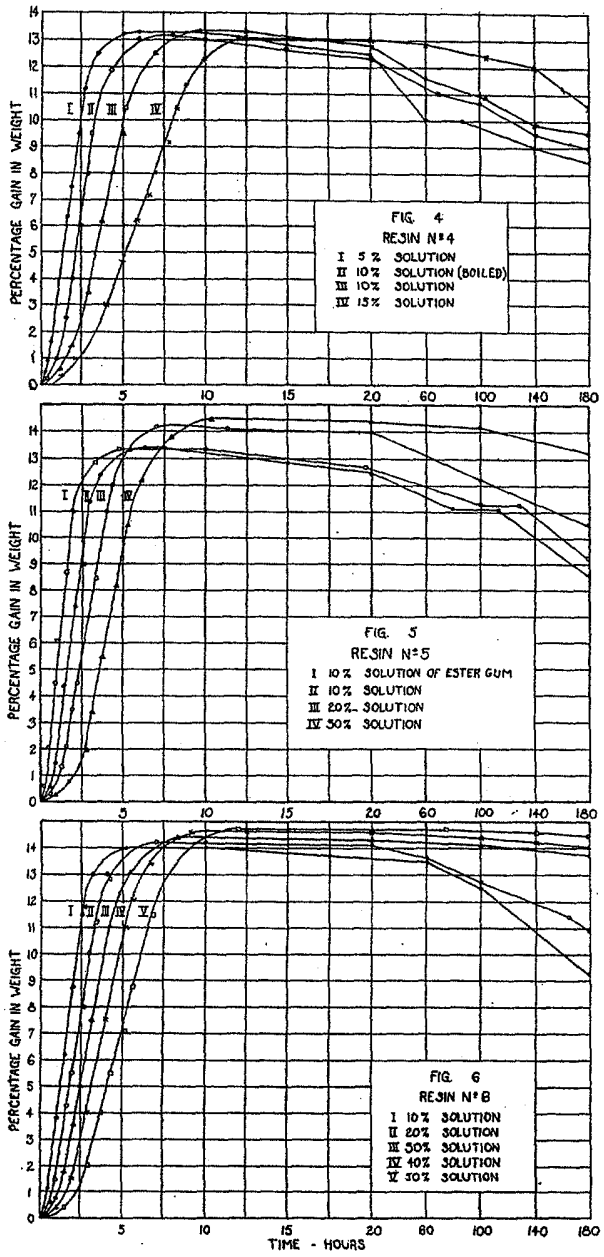
There was a loss in weight after the initial weighing in the higher concentrations of resin 1 and in all concentrations of resin 3. This portion of the curves was checked many times in an effort to determine the cause. It was found that heating the weighed sample of resin to incipient fusion under a vacuum before incorporation in the linseed oil resulted in the elimination of this behavior, without affecting the rest of the curve. Boiling weighed samples of resin in water, drying, and incorporating with oil had precisely the same effect. Naturally, there was a loss in weight of resin by both of these treatments. Some volatile water-soluble



substance was eliminated by these treatments, but it could not be identified with certainty, although occluded or adsorbed formaldehyde was suspected. Elm (2) noted a similar initial loss of weight in the drying of trilinolenic glyceride, which of course was not due to formaldehyde.

In order to test the applicability of Moureu and Dufraisse's theory to the work in hand, 4.0 grams of resins 1 and 3 were oxidized for one hour with 60 cc. of 30 per cent hydrogen peroxide. After thorough washing and drying, these samples were spread and weighed in the usual manner. Although the antioxygenic properties were not completely eliminated (Figure 1, I, and Figure 3, I), they were sufficiently decreased to substantiate the theory.

This same antioxidant effect was noted when commercial resins made up of mixtures of phenolic resins and ester gum were tested (Figures 4, 5, and 6). Ester gum itself was found slightly oxidizable, gaining 1.7 per cent in weight after



120 hours when spread as a film from an ether solution. It did not, however, show antioxidant properties when incorporated in linseed oil and treated in the usual manner (Figure 5, I). The synthetic resins did not gain in weight when treated in the same manner as the ester gum.

The amount of synthetic resin actually present in these solutions was less than the percentage given for the curves in the figures. Thus a 30 per cent solution of a 20 per cent phenolic resin–ester gum mixture actually contained but 6 per cent phenolic resin. Curves for such mixtures can scarcely be compared to 6 per cent solutions of purely phenolic resins, since the amount of oil exposed at the surface interface of the former was much less than that exposed in the latter case.

The temperature required to disperse resins 4 and 5 was 260° rather than 150° C. The curve for the linseed oil heated to 260° was identical with that heated to 150° within the limits of experimental error, and therefore was not included.

An interesting point concerning resin 4 was that it yielded, on prolonged treatment with boiling water, 19.93 per cent of 4,4-dihydroxydiphenylmethane. When this substance had been removed, the dried residue, incorporated in oil and spread in the usual manner, showed markedly less antioxidant effect (Figure 4, II). The other resins when so treated did not show any change in their antioxidant effect. With resin 3 an initial loss of weight was eliminated by this treatment, as has already been mentioned.

The increased viscosity of the solutions containing the larger amounts of resin was undoubtedly a factor in the rate at which the oil in the mixture absorbed oxygen, in that the diffusion of oxygen was rendered more difficult. No way of eliminating this was found. Then, too, there was less oil exposed at the surface of the more concentrated solutions, which would tend to slow up the oxygen absorption. It was believed that the slope of the curves representing more concentrated solutions was due at least in part to these factors.

Conclusion

The six phenol-formaldehyde resins and mixtures of these resins with ester gum studied in this investigation showed marked antioxidant effect on pure alkali-refined linseed oil in the presence of driers. This effect was specific for each individual resin, and was confined to the induction period. This antioxidant effect was partially due, in two cases, to some oxidizable part or component of the resin, since it was markedly decreased when the resin was treated with oxidizing agents. This last fact was in accord with the theory of Moureu and Dufraisse (*5*) relative to antioxygens, and indicated a possible treatment of such resins should their antioxygenic properties be undesirable.

The resins studied were apparently free from simple phenols used in their manufacture, although one of the resin–ester gum mixtures yielded a considerable amount of a complex phenol. The presence of free formaldehyde could not be demonstrated; yet in one case a behavior was noted which indicated the possibility of its presence.

The results of this investigation must not be compared to those attained with heat-bodied oils, since the oil used here was not heat-bodied. Neither must it be concluded that these resins prevented the complete drying of the oil, for the oil did dry eventually. The results of interest are those shown during the induction period of oxygen absorption.

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