

STUDIES ON REACTION OF RESINS WITH DRYING OILS

Part I.—Influence of Catalysts on the Reaction between Linseed Oil and Ester Gum

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(Received November 8, 1964)

The reaction between ester gum and linseed oil has been studied in the presence of catalysts such as litharge, manganese dioxide and cobalt acetate. Powers⁶ method has been used for evaluating the extent of reaction between resin and oil. The present investigations show that these catalysts and litharge in particular can influence the course of the reaction considerably and can therefore be used for the formulations of improved oleo-resinous varnishes.

Introduction

Oleo-resinous varnishes have been known for many centuries and their value for preservation and decoration is well established. Their preparation involves heating the resin and oil together at 300°C., this combination being the basic film-forming ingredient, and the final product is made from it by the addition of suitable thinners and driers. Varnish technology had, since its origin, been largely an art without much scientific understanding of its reactions or efficient control to maximise desirable properties. The usefulness of such coatings was increased greatly by the introduction of synthetic varnish resins and in particular the development of phenol-formaldehyde oil soluble resins around 1926. It was soon found that outstanding advantages of these phenolics depended on several factors such as type of phenol used¹⁻³ or the quantity of phenol-formaldehyde condensate incorporated in the resin.^{4,5} Since then attempts have been made to understand the reactions between resin and oil during the preparation of varnishes. It is now well recognised that the quality of the varnish depends on the extent of chemical combination that takes place between the two components.

Resin bodying of drying oils is a process involving colloid materials from the initial stage of the kettle to the final varnish and such systems are not easy to examine by chemical methods. Powers⁶ has shown that useful information in this respect can be obtained by plotting logarithm of viscosity against cooking time. If the slope of the curve is substantially the same as for linseed oil, it would show that resin has increased the initial viscosity of the oil, which then bodies at the expected rate and little reaction takes place bet-

ween resin and oil. Powers has thus shown that there is practically no reaction between ester gum and linseed oil. In the case of oil-soluble phenolics, the viscosity decreases during the first two hours and then rises at a very rapid rate, which suggests considerable reaction between the phenolic resin and linseed oil. This explains why these resins greatly surpass in performance the earlier types.

The influence of catalysts on the reaction between resin and oil does not appear to have been studied. The present work was undertaken to study the influence of litharge, manganese dioxide and cobalt acetate on the reaction between ester gum and linseed oil by using Powers' technique for assessing the reaction between resin and oil.

Preliminary Experiments

A few preliminary experiments were carried out by cooking linseed oil (250 g.) and ester gum (250 g.) at $300 \pm 2^\circ\text{C}$. under the following conditions (1) in a three-necked flask fitted with mechanical stirrer, thermometer and inlet for carbon dioxide so as to maintain an inert atmosphere, (2) in an open beaker with mechanical agitation and (3) in an open beaker with mechanical agitation after incorporation of 0.5 percent litharge by weight of oil. In all these cases, samples were withdrawn at regular intervals, diluted with mineral turpentine in the ratio of 4:1 and examined for viscosity by the bubble tube method. The results are shown in Fig. 1(a), which show the comparative faster rise of viscosity in the case of varnishes prepared in an open beaker. Varnishes prepared in the open beaker had better drying

qualities but were otherwise inferior to those prepared in an inert atmosphere. It was therefore decided to study the oil-resin reaction in an atmosphere of carbon dioxide and to measure the viscosities after diluting the varnish in the ratio of 9:1 so as to extend the range of viscosities for better evaluations of the influence of catalyst.

Influence of Catalysts

Oleo-resinous varnishes were prepared as described earlier in an atmosphere of carbon dioxide. The catalysts were incorporated at 250°C. and runs were made with (1) no catalyst, (2) 0.5 percent litharge, (3) 0.5 percent litharge and 0.2 percent manganese dioxide, (4) 0.2 percent manganese dioxide and (5) 0.1 percent cobalt

acetate. The proportion of the catalysts indicated in all the cases is by weight of the oil. The results are shown in Figs. 1(b) and 2(a) from which it can be observed that there are three stages of the resin-oil reaction where catalysts have been used, whereas there are only two stages in the absence of any catalyst. With litharge, during the first stage, there is a rapid rise in viscosity, during the second stage the viscosity remains almost at the same level with a slight depression towards the end and in the third stage there is again a rapid increase, of viscosity. When a mixture of litharge and manganese dioxide is used, the pattern remains the same but the viscosity rise in the first stage is comparatively greater. With manganese dioxide or cobalt acetate, the behaviour is almost identical. During the first stage, rate of increase in viscosity is faster and again increases during the final stage. These results show that the catalysts can be helpful in inducing reaction between resin and oil. Slight depression obtained during the second stage with litharge was studied further with more accurate measurements.

Accurate Measurements

For the final study of linseed oil-ester gum reaction in the presence of litharge, the viscosity was measured at 60°C. on undiluted samples. Their molecular weight and acid values were also determined.

(1) Measurement of viscosity was carried out by an Ostwald type viscometer (B.S.S. No. 4). The time of flow from which the viscosity of the sample was calculated was the average of two readings. The measurement was carried out at 60°C., the thermostat used in the experiment giving an accuracy in control of temperature of $\pm 0.01^\circ\text{C}$.

(2) Molecular weight determination was carried out in the Mechro-Laboratory Model 301 A Osmometer. For this purpose the solutions of the samples were prepared in dry benzene and each determination was carried out on two different concentrations and three readings were taken for each concentration.

(3) Acid value was determined on 1 g. samples dissolved in benzene against standard alcoholic sodium hydroxide solution.

The results shown in Figs. 2(b) and 3 confirm that there is a depression in viscosity during the second stage. This is due to decrease in molecular weight during this period which in turn is due to

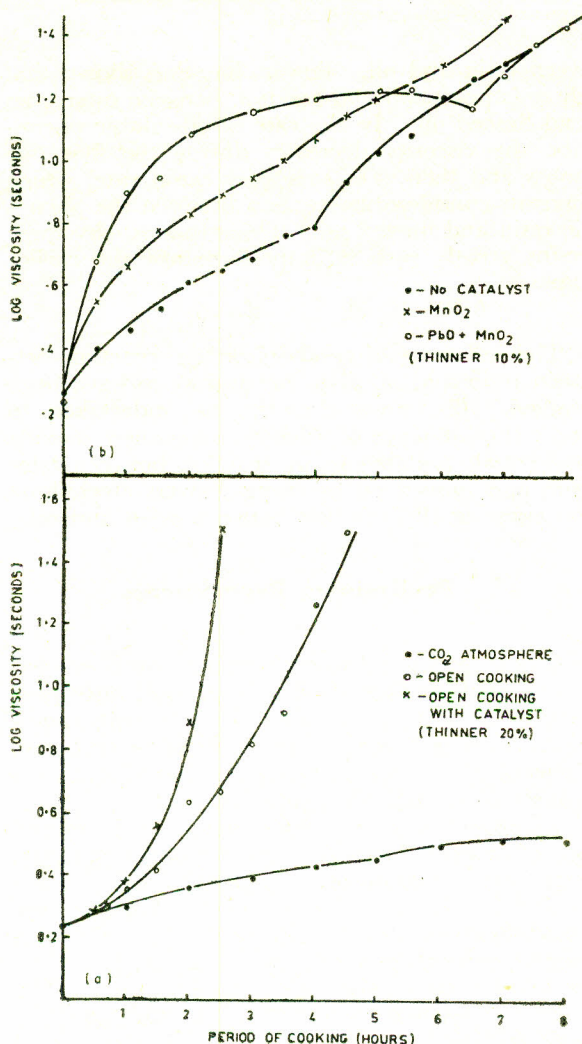


Fig. 1.—Showing relationship between period of cooking and log viscosity (seconds).

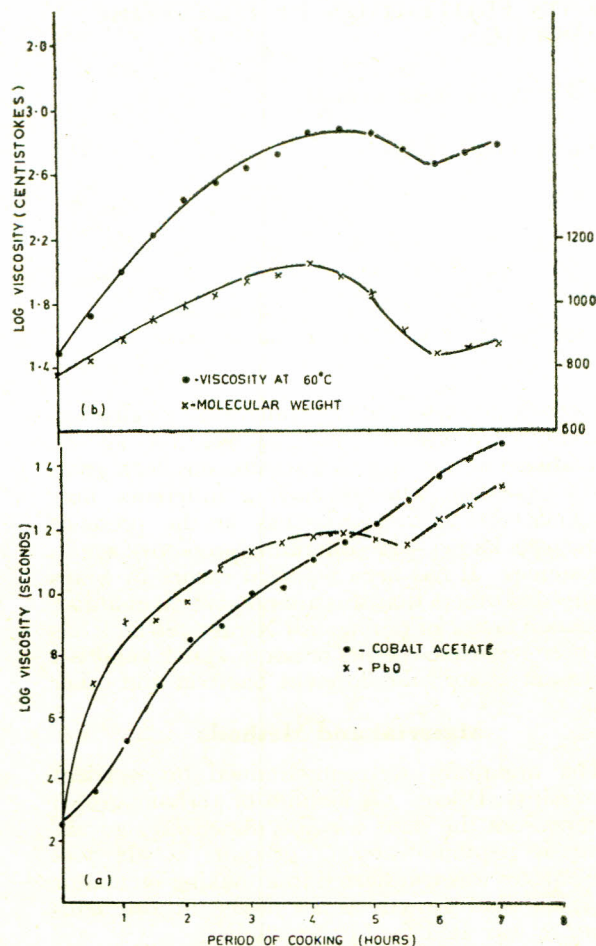


Fig. 2.—Showing relationship between period of cooking and (a) log viscosity (seconds) (b) log viscosity (millipoises) and molecular weight.

sudden rise in free fatty acids. In the absence of catalyst, the acid value remains more or less the same.

Conclusion

The reaction between ester gum and linseed oil has been studied in the presence of catalysts. The

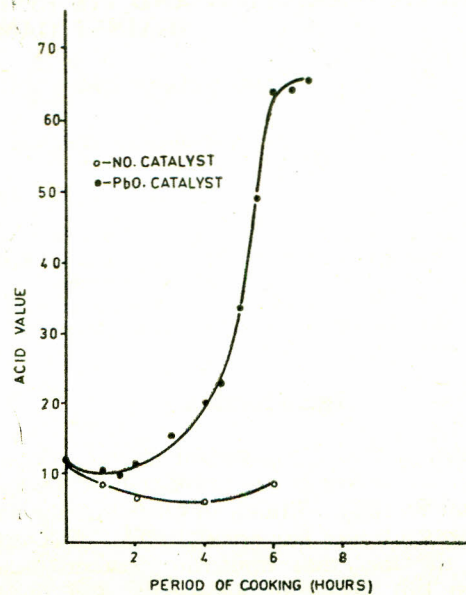


Fig. 3.—Showing relationship between acid value and period of cooking.

present investigations show that the catalysts can influence the course of the reaction considerably and therefore can play an important role in the formulation of improved oleo-resinous varnishes. Further work is in progress.

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