

**Part II.—Influence of Catalysts on the Reaction between Linseed Oil and Pentaerythritol Rosin Ester**

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Reaction between pentaerythritol — rosin ester and linseed oil has been studied in the presence of catalysts such as litharge, manganese dioxide and cobalt acetate. The present investigations have confirmed the previous findings that catalysts play a significant role in the oil-resin reactions during the preparation of oleo-resin varnishes. The most significant result of the present investigations is that whereas the catalysts accelerate the rate of polymerisation in case of linseed oil and linseed oil-ester gum based varnishes, it has just the opposite effect in case of linseed oil-pentaerythritol rosin ester, coatings. This indicates that if more reactive components are used in the manufacture of varnish, it should be possible to prepare improved coatings, with the use of catalysts to alter the course of oil-resin reaction.

### Introduction

In a previous communication,<sup>1</sup> it was reported that catalysts and particularly litharge exercises significant influence on the course of the reaction between ester gum and linseed oil during the preparation of oleo resinous varnishes. It was, therefore, thought worthwhile to extend this study to reaction between pentaerythritol ester of rosin and linseed oil and the results of these investigations are reported in this paper.

### Experimental

Linseed oil (1000 g.) and pentaerythritol (1000 g.) were heated in a four-necked flask fitted with mechanical stirrer, thermometer and inlet for carbon dioxide so as to maintain an inert atmosphere. The catalysts were incorporated at 250°C., the temperature of the mass raised to 300°C. and cooking continued at this temperature. Samples were drawn at fixed intervals for measurement of viscosity, molecular weight, refractive index, acid value, and film forming properties.

Measurement of viscosity was carried out using an Ostwald type viscometer (B.S. No. 4) at  $60 \pm 0.01^\circ\text{C}$ . Molecular weight determination was carried out in the Meckro-Laboratory Model 301A osmometer. Refractive index was determined at 60°C. using Abbes refractometer (Zeiss Optim Co., Germany).

Acid value was determined by dissolving 1 g. sample in benzene against standard alcoholic sodium hydroxide solution. The drying proper-

ties of the film was assessed by hand-touch and expressed as time taken by the film to (a) dry-to-touch (b) become hard-dry and (c) become tack-free. The remaining tests were carried out after one week of the application of film. Scratch hardness was determined on the standard scratch test apparatus. Resistance of film to water was judged by (1) impregnating thin paper with varnish and estimating water absorption in 24 hours (2) noting the time taken by the film to become hazy.

### Results and Discussion

Litharge, manganese dioxide and cobalt acetate, in proportion of 0.5%, 0.2% and 0.1% by weight of oil, respectively were used for the present study. Influence of these catalysts with linseed oil alone was also studied as control.

Data in respect of changes in viscosity, molecular weight and refractive index with period of cooking for linseed oil-pentaerythritol varnish is shown in Fig. 1. Similar data for linseed oil is shown in Fig. 2. Data relating to film forming properties is given in Table 1.

Significant results from the present study are:

- (1) Incorporation of catalysts in case of linseed oil increases the rate of polymerisation, the efficiency of the catalysts in order of merit being litharge, cobalt acetate and manganese dioxide. Similar results were obtained in the earlier work with linseed-ester gum reaction though with litharge, the reaction went

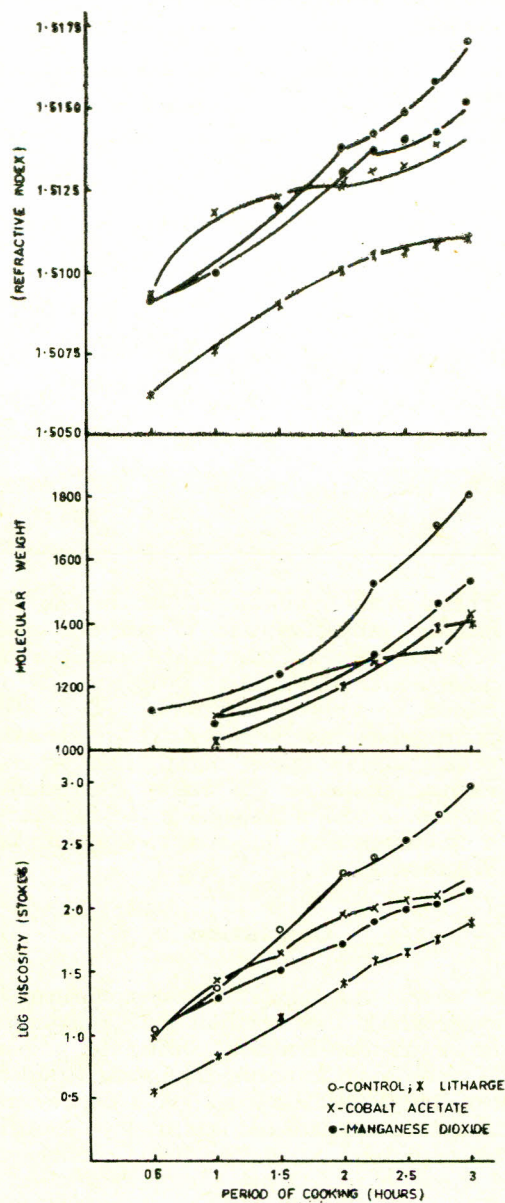


Fig. 1—Showing relationship between period of cooking and (a) log viscosity in stokes, (b) molecular weight and (c) refractive index for linseed oil-pentaerythritol rosin ester.

through three stages—viscosity rises rapidly during the first stage, reaches a steady level and decreases during second stage and again rises during the third stage. This depression in second stage was found to be due to sudden rise in fatty acids during the period resulting in lowering of molecular weight. In case of linseed oil-pentaerythritol ester, the most

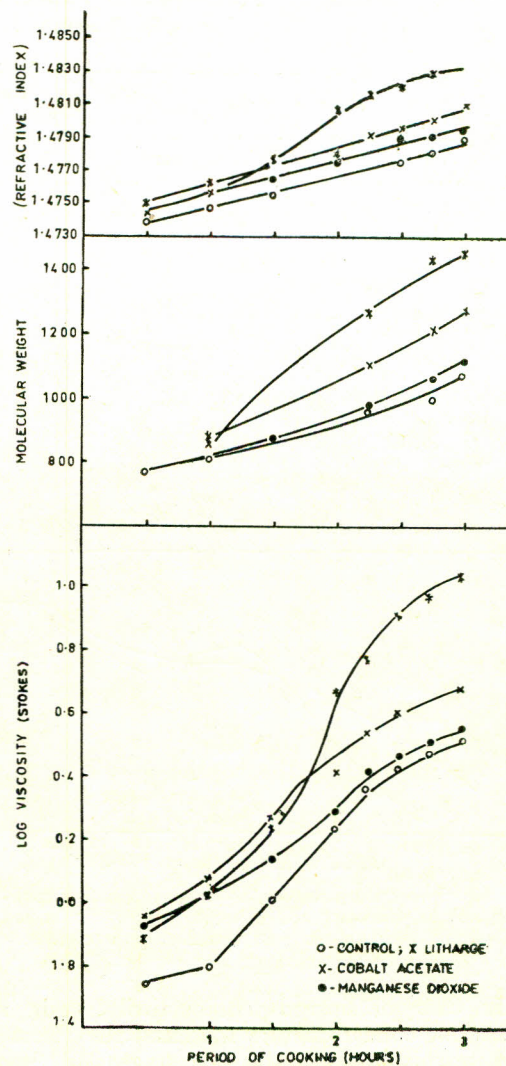


Fig. 2—Showing relationship between period of cooking and (a) log viscosity in stokes, (b) molecular weight and (c) refractive index for linseed oil.

remarkable observation is that all the catalysts depress the rise of viscosity and litharge in particular depresses, to a greater extent, than other catalysts. Furthermore, in this case, no rise in acidity was observed. Influence of litharge was then studied for over a longer duration. It was found (Fig. 3) that in this case also, there is a depression of viscosity and molecular weight during the second stage. Since there is no rise of free acidity, this depression can be attributed only to greater interaction between resin and oil.

TABLE I.—FILM-FORMING PROPERTIES OF LINSEED OIL-PENTAERYTHRITOL ROSIN ESTER COATINGS.

Period of cooking	Water absorption %				Time taken by film to become hazy (hours)				Scratch value			
	Control	Pb	Co.	Mn.	C	Pb	Co	Mn	C	Pb	Co	Mn
0.5	1.75	1.80	1.80	1.61	3.0	3.0	3.5	4.0	500	500	400	400
1.0	1.62	1.78	1.80	1.41	3.5	3.5	4.0	4.5	600	600	450	500
1.5	1.58	1.50	1.78	0.70	4.5	4.5	5.0	5.5	700	700	500	600
2.0	1.56	1.35	1.68	0.69	6.0	6.0	5.5	6.5	700	750	550	650
2.25	0.85	0.98	1.62	0.68	8.0	8.0	6.0	8.5	750	800	600	750
2.50	0.82	0.87	1.41	0.68	9.5	9.5	7.5	11.0	800	950	750	752
2.75	0.78	0.78	1.10	0.68	10.0	10.0	10.0	12.5	950	1000	750	852
3.0	0.73	0.75	0.71	0.68	14.0	14.0	11.5	14.5	1000	1000	800	950

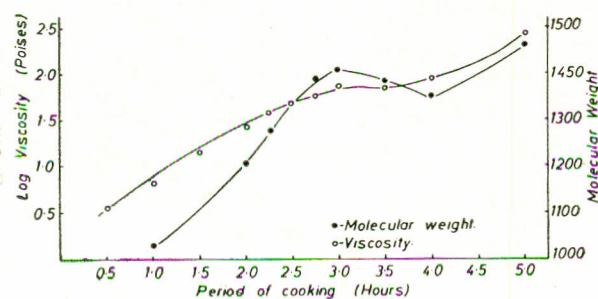


Fig. 3—Showing relationship between period of cooking and log viscosity and molecular weight for linseed oil-pentaerythritol rosin ester with litharge as catalyst.

- (2) In case of linseed-pentaerythritol resin reaction, cobalt acetate increases the viscosity of varnish during the first stage and thereafter exercises little influence on the course of the reaction. The initial higher viscosity is not due to greater increase in molecular weight as can be seen from Fig. 1 (b). This initial rise could be due to either colloidal formation of cobalt oxide or greater isomerisation of the oil as can be seen by the rapid increase of refractive index or both. Even in the case of linseed oil, cobalt oxide is more effective in increasing the refractive index during the first stage.
- (3) In case of linseed oil, manganese dioxide has a slight accelerating influence but in case of linseed oil-pentaerythritol varnish, its effect is more pronounced than cobalt acetate.

- (4) There is no significant change in the film-forming properties due to use of various catalysts, except that when catalysts are used, better film-forming properties are obtained at reduced viscosities. Two other points which may be noted are (1) the use of cobalt acetate gives slightly inferior film-forming properties (2) water absorption of the film in case of manganese dioxide reaches a minimum after one-hour cooking and then stays steady.

### Conclusion

The present investigations have confirmed the previous findings that catalysts play a significant role in the oil-resin reactions during the preparation of oleo-resin varnishes. The most significant result of the present investigation is that whereas the catalysts accelerate the rate of polymerisation in case of linseed oil and linseed oil ester gum based varnishes, it has just the opposite effect in case of linseed oil-pentaerythritol rosin ester coatings. This indicates that if more reactive components are used in the manufacture of varnish, it should be possible to prepare improved coatings, with the use of catalysts to alter the course of oil-resin reaction.

### Reference

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