

STUDIES ON THE INFLUENCE OF THE METHODS OF PREPARING MALEIC RESINS ON THEIR APPLICATION IN SURFACE COATINGS

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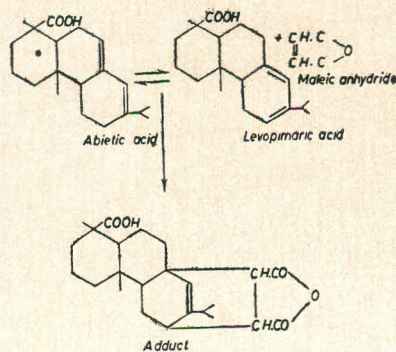
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(Received October 30, 1961)

This paper deals with the various methods of preparing oil soluble maleic resins and their influence on the properties of these resins with respect to their application in surface coatings. Best results are obtained when the three ingredients—rosin, maleic anhydride and glycerol—are reacted under conditions which give the maximum polymerisation, without making the product insoluble in oil. It has been found that this can be achieved by reacting maleic anhydride with a full quantity of glycerol at 200–10°C. for 30 minutes, incorporating rosin and heating the mass at 270–80°C. till there is no further reduction in acid value. Resins thus prepared have higher melting points as well as improved water resistance, and have merely to be dissolved in drying oils for the preparation of oleo-resinous varnishes.

Introduction

The two outstanding properties which have made maleic resins occupy a unique place in the surface coatings are: (i) the light colour and comparative freedom from yellowing which is a characteristic of phenolic resins, and (ii) extreme compatibility with nitrocellulose in the manufacture of lacquers, whereas pentaerythritol resins, which are formidable competitors of maleics in the varnish field, are incompatible. The preparation of maleic resins by reacting together rosin, maleic anhydride, and glycerol was first described by Carleton Ellis.¹ Theoretically three types of reactions are involved in this preparation: (1) esterification of the dibasic and monobasic acids by the polyhydric alcohol, (2) formation of the adduct of maleic anhydride with the rosin acids by an addition reaction,² akin to Diels-Alder reaction as shown below:—



(3) Condensation reaction between maleic anhydride and glycerol in accordance with Kienles' concepts of functionality. The reactivity of the ingredients being 4:3, the tendency would be to form chains. These chains would react with one another to form a highly complex three-dimensional pattern and on heating yield a infusible and insoluble material. Which of these reactions will

predominate will depend on the method used for the preparation of these resins. Various methods for the preparation have been suggested, but there is no information available on the influence of the method of preparation on the properties of the resins in respect of its applications in surface coatings. The results of investigations carried out on this subject are presented in this paper. This work is limited to resins which are oil-soluble and do not contain more than 10% of maleic anhydride by weight of rosin. Larger quantities of maleic anhydride are reported to give oil-insoluble resins suitable for incorporating in nitrocellulose based lacquers.

Preparation of Maleic Resins

The preparation of the resins was carried out in a 4-necked flask equipped with a constant speed glass stirrer, thermometer, inlet for carbon dioxide (used to maintain inert atmosphere in the flask) and a distillation connection to remove the water as it is formed. All connections were made with standard taper ground glass joints and heat was applied by a heating mantle regulated by a variac. The following methods of preparation were studied:—

1. Rosin and maleic anhydride are charged into the reaction flask, heated to 210°C. and maintained at this temperature for 30 minutes to facilitate the formation of the adduct. The temperature is raised to 270–80°C., and glycerol introduced gradually into the flask to esterify the adduct.

2. Preliminary experiments had shown that maleic anhydride (3 moles) and glycerol (2 moles) on heating to 200°C. for 20 minutes led to the formation of an infusible resin and this could be prevented by incorporating rosin (two times the weight of maleic anhydride) in the initial stages. Glycerol, maleic anhydride and the quantity of

rosin required to prevent the formation of infusible mass, are heated together at 200°C. for 30 minutes. Balance quantity of rosin is then introduced and the resultant product finally esterified with glycerol at 270-280°C.

3. Ester gum is heated with maleic anhydride at 200-10°C. for 30 minutes and the resultant product treated with glycerine at 210-220°C.

4. Rosin, maleic anhydride and glycerol are charged in the reaction flask and heated together at 270-280°C. till no further reduction in acid value is obtained.

5. Maleic anhydride and the full quantity of glycerol (including what is required for esterification of rosin) are heated at 200-10°C. for 30 minutes. Rosin is introduced and the resultant mixture heated at 270-280°C. till there is no further reduction in the acid value of the product.

6. Part of rosin, maleic anhydride and the full quantity of glycerol (including what is required for esterification of rosin) are heated at 200-10°C. for 30 minutes. The balance quantity of rosin is introduced and the resultant mass heated at 270-280°C. till there is no further reduction in acid value.

In all the above preparations, 0.5% zinc oxide by weight of rosin was used as catalyst for esterification of rosin and incorporated into the formulation at 230-240°C.

The details of the formulations and the values for acid value and melting points of the maleic resins prepared by different methods are reported in Table 1. One resin from each group (Resin Nos. 1, 7, 8, 9, 11 and 16) was selected for the study of:—

(a) Viscosity of the resins in mineral turpentine (1:1 by weight) turpentine oil and linseed oil (2:1 by weight) by bubble tube method. The results are given in Table 2.

(b) Water resistance of straight resin films by flowing 66% solution of resins in a solvent on to a tin panel, allowing it to dry for 24 hours, and immersing the panels in water. Observations on physical defects during three days immersion are given in Table 3.

Film Forming Properties

Linseed oil varnish of 12½ gallons oil length (oil length signifies gallons of oil per 100 lbs. of the resin) was selected for studies in film formation and equivalent standard was prepared using ester gum.

TABLE 1.—FORMULATIONS AND PROPERTIES OF MALEIC RESINS.

Resin No.	Raw Materials			Finished product	
	Rosin (g.)	Maleic anhydride (g.)	Glycerol (ml.)	Acid value	Melting point °C (capillary method).
<i>Method (1)</i>					
1	.. 300	30	55	32.0	120-22
2	.. 300	30	48	34.1	122-24
3	.. 300	30	60	28.5	122-24
4	.. 300	22.5	45	33.5	110
5	.. 300	15.0	40	24.6	102
<i>Method (2)</i>					
6	.. 60+240	30	18+30	31.0	128-30
7	.. 60+240	30	21+29	26.9	128-30
<i>Method (3)</i>					
8	.. 300 (ester gum)	30	18	36.2	120-22
<i>Method (4)</i>					
9	.. 300	30	48	27.5	122-24
<i>Method (5)</i>					
11	.. 300	30	50	18.0	128-30
12	.. 300	22.5	45	19.1	118-20
13	.. 300	15	40	19.2	105-06
<i>Method (6)</i>					
14	.. 120+180	30	48	24.9	—
15	.. 60+240	30	48	23.0	125-26
16	.. 30+270	30	48	19.6	—
17	.. 30+270	30	50	20.3	125-26
18	.. 30+270	22.5	45	20.2	118
19	.. 30+270	15.0	40	18.2	105-06

TABLE 2.—VISCOSITY OF RESIN SOLUTIONS.

Resin No.	Viscosity of resin solutions in		
	Mineral turpentine	Turpentine oil	Linseed oil
1	.. 4.8 Seconds	4.7 Seconds	8.2 Seconds
7	.. —	5.5 "	10.2 "
8	.. —	5.2 "	7.1 "
9	.. 5.3	6.2 "	11.0 "
11	.. —	7.4 "	18.4 "
16	.. 5.4	6.5 "	12.5 "
Ester gum	.. —	—	7.1 "

TABLE 3.—COLD WATER IMMERSION TESTS ON STRAIGHT RESIN FILMS.

Resin No.	Blushing after immersion in cold water for			
	12 hours	36 hours	60 hours	72 hours
1	None	Slight	Moderate	Moderate
7	None	Slight	Moderate	Moderate
8	None	Slight to moderate	Moderate to severe	Severe
9	None	None	Slight	Slight to moderate
11	None	Very slight	Slight	Slight to moderate
16	None	Very slight	Slight	Moderate

TABLE 4.—DRYING TIME (IN HOURS) OF VARNISHES.

Resin No.	Drying properties after		
	1 hr.	2 hrs.	3 hrs. (cooking period)
1	48	48	48
11	36	36	36
16	36	36	24

TABLE 5.—SCRATCH HARDNESS OF VARNISHES.

Cooking period (hrs.)	Scratch hardness			
	Resin I	Resin 11	Resin 16	Ester gum
1	850	1050	900	700
2	850	1050	900	850
3	1000	1050	1100	700
4	950	850	1100	650
5	850	750	900	650
6	650	750	900	650

In making the linseed oil varnish, the resin (150 g.) and the oil (150 g.) are charged in a beaker and heated together to 240°C. Litharge (0.645 g.) is added and the temperature raised to 290°C. Manganese dioxide (0.475 g.) is then added and the cooking temperature maintained at 290-300°C. Samples are drawn every half an hour to determine the polymerisation rates of the varnishes. For this the varnishes are adjusted to a solids content of 66.0% and the viscosity determined at 30°C. by bubble-tube method. These results are shown in Fig. 1. The drying properties of these varnishes at different stages have been assessed by touching with the finger at regular intervals after application and the time taken for the films to become tack-free (all at room temperature) are reported in Table 4. The values for scratch hardness of varnish films are given in Table 5.

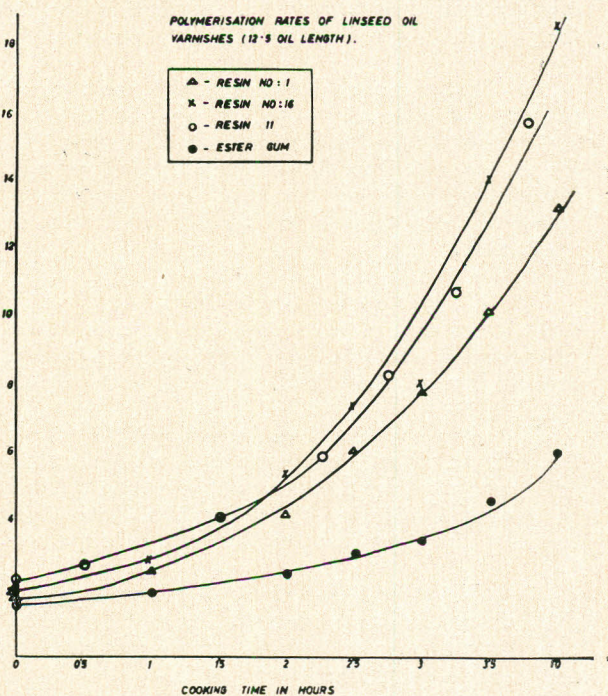


Fig. 1.—Polymerisation rates of linseed oil varnishes (12.5 oil length).

Conclusion

It has been found that the method of preparation has considerable influence on the properties of the maleic resins. One of the prerequisites for resins used for surface coatings is that their acid value should be less than 20. Resins prepared according to methods 5 (Resin 11) and 6 (Resin 16) fulfil this primary condition and furthermore have better water-resistance properties, probably due to their higher degree of polymerisation as

judged by the higher viscosities of the resin solutions. The addition of the total quantity of glycerol (including the quantity required for the esterification of rosin) in the beginning reduces the possibility of the formation of over-polymerised insoluble and unusable polymer of glyceryl maleate. On the other hand, the incorporation of a part of the rosin in the beginning in accordance with method 6, has a diluting effect which slows down the polymerisation rate of glyceryl maleate. Resin 11 is therefore more polymerised and comparatively better than Resin 16.

The bodying rate of the linseed oil varnishes made with Resins 11 and 16 is practically of the

same order and better than Resin 1 and Ester gum. Whereas Resin 11 has merely to be dissolved in linseed oil to give a satisfactory varnish, other resins require 1-2 hours cooking time to secure the desirable properties. To conclude, Resin 11 prepared in accordance with method 5, is the best of all the maleic resins prepared during the present investigation.

References

1. Carleton Ellis, U. S. Patent 1,722,566.
2. A. G. Harvey and T. S. Hodgins Ind. Eng. Chem., **32**, 272 (1940).