USE OF MALEIC ANHYDRIDE FOR EXTENDING THE OIL-LENGTH OF COTTONSEED OIL-BASED OLEO-RESINOUS VARNISHES

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Incorporation of maleic anhydride by 'in-situ' technique is useful in increasing the oil/resin ratio of cottonseed oil-based coating compositions from 1.25 to 3.0. Varnishes prepared with an oil/resin ratio of 2.0 and maleic anhydride 7.5% by weight of the oil have superior film forming properties. The use of maleic anhydride-modified rosin esters with ordinary or maleinised cottonseed oil is not successful for extending the oil length of these varnishes.

Introduction

Earlier work reported from these laboratories[1] has shown that cottonseed oil can be used for the preparation of oleo-resinous varnishes by judicious control of catalysts and the degree of polymerisation. The maximum proportion of oil that can be used in these formulations is 1.25 parts of oil to 1.00 parts of rosin and there is thus a need to develop methods for preparing varnishes of longer oil-length. Maleic anhydride is known to improve the drying properties of semi-drying oils,[2,3] for example soyabean oil, (iodine value 134) when cooked with 5-10% maleic anhydride, gives hard and dry, though not tack-free, film in 48-72 hours. On the other hand, maleic anhydride reacts with rosin to form adducts which have improved film-forming properties. Incorporation of maleic anhydride in the cottonseed oil-based varnishes is therefore most likely to give the desired results by yielding improved coating compositions. The use of maleic anhydride for extending the oil-length of these varnishes has been investigated and the results of the study are reported in this paper. The following types of varnishes have been chosen for the present study: (A) those in which maleic anhydride is allowed to react simultaneously with oil and rosin (in-situ method) and the acidity is then reduced with metallic oxides or glycerol or a mixture of both, (B) those in which maleic anhydride-modified rosin ester is processed with the oil, and finally (C) those in which maleic anhydride modified-rosin ester is processed with maleinised oil.

Experimental

Preparation of Maleic Anhydride-modified Rosin Ester.—This resin was prepared according to Method(1) described in the work on maleic resins reported from these laboratories.[4]

Preparation of Varnishes.—Type A: Method (1): A mixture consisting of rosin, maleic anhydride and a portion of cottonseed oil (generally 25% by weight of rosin) was processed in a open beaker with agitation, at a temperature of 200-210°C. for about 30 minutes. The temperature was then raised to 240-250°C. and the oxides incorporated in the following order: calcium hydroxide, zinc oxide, litharge and manganese dioxide. After the addition of oxides, balance quantity of oil was added and the temperature raised to 300-310°C. Cooking was continued at this temperature and samples drawn from time to time for evaluation of physical properties. Method (2): A mixture consisting of rosin, maleic anhydride and cottonseed oil was processed at 200-210°C. as in method (1). The mass was heated to 270-280°C. and maintained at that temperature while the catalyst was introduced and glycerol added in instalments. After the esterification had been substantially completed, the balance quantity of oil was added, litharge and manganese dioxide incorporated, and the temperature raised to 300-310°C. The rest of the procedure was the same as described in method(1).

Type B:—A mixture consisting of Maleic-modified rosin ester and cottonseed oil was heated to 240-250°C., litharge and manganese dioxide incorporated and the temperture raised to 300-310°C. Heating was continued at this temperature and samples drawn at regular intervals for examination.

Type C:—A mixture consisting of cottonseed oil and maleic anhydride was processed at 200-210°C. for about 30 minutes. Maleic anhydride-modified rosin ester was incorporated and the resulting mix was processed as in Type B.

The varnishes were evaluated for acid value, viscosity, drying poperties, scratch hardness and water resistance. The methods used were the same as described in the earlier publication.[1]

Results

Data in respect of the formulations studied are given in Table 1, physical properties of these varnishes in Table 2 and their water-resistance properties in Table 3. These results show that the method described for the preparation of varnish belonging to Type A can be used to prepare tack-free Oleo-resinous varnishes of oil/resin ratio of 3:1. In general, varnishes in which acidity of rosin is reduced substantially by glycerol are far superior to those in which metallic oxides are used for neutralisation of the acidity. In particular, formulation No. 2 using oil-resin ratio of 2:1 and maleic anhydride 7.5% by weight of oil gives excellent results. Its scratch hardness value is of the order of 650 as against 280 reported for the best cottonseed varnish prepared without the incorporation of maleic anhydride.[1] Methods used for preparation of varnishes belonging to Types B and C, considerably improve their film-forming properties particularly in respect of scratch hardness but are not useful for extending their oil-length.

TABLE 1.—FORMULATIONS OF COTTONSEED OIL-BASED VARNISHES.

Varnish No.	Oil/resin ratio	Maleic anhydride % by weight of oil	PbO% by weight of oil	MnO_2% by weight of oil	CaO% by weight of rosin	ZnO% by weight of rosin	Glycerol % by weight of rosin
1. Type A	2:1	7.5	1.0	0.5	7.0	—	—
2. ,, ,,	2:1	7.5	1.0	0.5	—	0.5	12.5
3. ,, ,,	2:1	20.0	1.0	0.5	—	0.5	24.0
4. ,, ,,	3:1	7.5	1.0	0.5	—	0.5	12.5
5. ,, ,,	3:1	7.5	1.0	0.5	7.0	—	—
6. ,, ,,	5:1	7.5	1.0	0.5	7.0	—	—
7. ,, ,,	5:1	10.0	1.0	0.5	—	0.5	25.0
8. Type B	1:1	—	1.0	0.5	—	—	—
9. ,, ,,	2:1	—	1.0	0.5	—	—	—
10. ,, C	2:1	5.0	1.0	0.5	—	—	—
11. ,, B	3:1	—	1.0	0.5	—	—	—
12. ,, ,,	5:1	—	1.0	0.5	—	—	—

TABLE 2.—PHYSICAL PROPERTIES OF COTTONSEED OIL-BASED VARNISH FILMS.

Varnish No.	Volatile content of varnish adjusted to viscosity of 6.0 poises at 30° C.	Time for the film to			Scratch resistance	Acid value
		Touch dry Hours	Hard dry Hours	Tack free Hours		
1.	75.0	1	24	48	250–270	7.5
2. (a)	52.5	6–8	24	48	450–500	8.8
2. (b)	60.0	$1\frac{1}{2}$	4–6	24	600–650	8.6
2. (c)	72.8	3/4	2	24	650–700	7.1
3	60.0	$3\frac{1}{2}$	10–12	24	550–570	15.2
4	44.2	12—14	24	72	200–220	12.4
5	64.0	4-5	12	36	180–200	18.6
6	50.0	18—20	48	does not become tack-free		16.5
7	—	48	does not become hard dry or tack-free			15.6
8	45.0	2	6-8	24	900–950	—
9	60.5	12	96	does not become tack-free		—
10	58.5	8	72	does not become tack-free		—
11	56.0	48	does not become hard dry or tack-free			—
12	55.4	does not dry at all				

TABLE 3.—COLD WATER IMMERSION TESTS.

Material under test (Varnish No.)	Blushing after immersion in cold water for		
	1 hour	4 hours	24 hours
1	moderate	moderate to severe	severe
2 (a)	slight	slight to moderate	moderate
2 (b)	unaffected	unaffected	slight
2 (c)	unaffected	unaffected	slight
3	very slight	slight	slight to moderate
4	slight to moderate	moderate	moderate to severe
5	moderate	moderate to severe	severe
8	slight	slight to moderate	moderate
9	moderate	moderate to severe	severe

The relationship between cooking time and logarithm of viscosity for varnishes of oil-resin ratio of 2:1 as shown in Fig. 1 is significant.

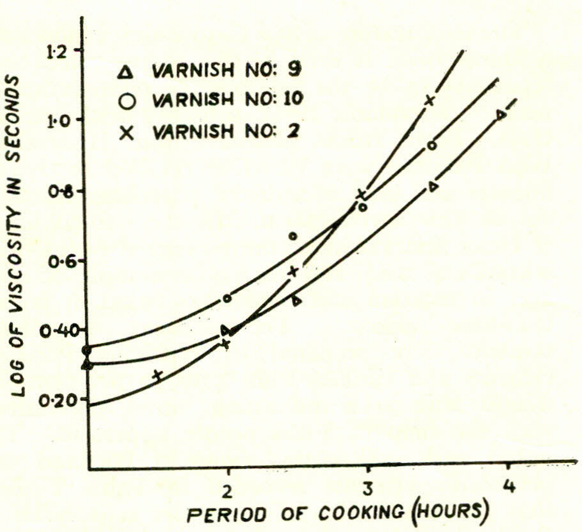

Fig. 1 —Showing polymerisation of different types of varnishes.

The curve for varnish No. 9 using maleic resin follows a common pattern for any varnish preparation. The use of maleinised oil for varnish No. 10 increases the initial viscosity but does not alter the rate of polymerisation since the curve for No. 10 runs almost parallel to that for No. 9. On the other hand, varnish No. 2 has a lower viscosity to start with but shows a considerably higher rate of polymerisation. This is probably due to greater degree of co-polymerisation between the resin and oil and explains why 'in-situ' technique of heating maleic anhydride, rosin and oil is helpful in extending the oil-length of the cottonseed oil-based coating composition and improving their water-resistance properties.

The properties of the varnish further depend on the extent of polymerisation. This can be seen from the data for physical properties of films for formulation No. 2 in Table 2. Another interesting result is that the use of maleic anhydride in the proportion of 7.5% by weight of the oil is sufficient and any increase does not lead to further improvement in film-forming properties.

Conclusions

It has been possible to extend the oil/resin ratio of cottonseed oil-based varnishes from 1.25 to 3.0 by incorporation of 7.5% maleic anhydride by weight of the oil and using 'in-situ' technique. However, varnishes prepared with an oil-resin ratio of 2.0 have the best film-forming properties. The use of maleic anhydride-modified rosin ester with unmodified or maleinised cottonseed oil is not helpful in extending the oil-length of the varnishes, but does give superior film-forming properties.

References

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