

PREPARATION OF LINSEED FATTY ACIDS-BETULINOL ESTERS AND THEIR EVALUATION AS PROTECTIVE COATING VEHICLES

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This paper deals with a new series of esters prepared by condensation of linseed fatty acids with betulinol and extracts of *Betula utilis* (Bhojputr) at 270-80°C. These compounds have longer induction period but ultimately become tack-free in a shorter period as compared with linseed oil. Esters prepared by partial reduction in acid value by extracts of *Betula utilis* and subsequent reaction with glycerol or pentaerythritol are the best in this series. The bodying characteristics and varnish-making qualities of these esters have also been studied. On the whole these esters are better than linseed oil for use in coating compositions.

Introduction

It is well known that the higher fatty acids can be readily esterified with alcohols by direct condensation at 180-200°C. This reaction has been made use of by re-esterifying the crude fatty acids of drying oils with polyhydric alcohols containing three or more hydroxyl groups. With the increase of complexity of alcohol, the rate of drying and the hardness of the film is correspondingly increased. For example, the glyceryl ester of linseed oil is better than raw oil in respect of having a shorter induction period and the pentaerythritol ester is superior in all respects. The use of meso-inositol,¹ a cyclic hexahydric alcohol, containing only secondary hydroxy groups, is also reported to give a product which compares favourably with the pentaerythritol ester. Recent work carried out at these laboratories has shown² that fatty acids can be directly esterified with betulinol or extracts of *Betula utilis* (Bhojputr) as such but slightly higher temperatures are needed for bringing about the esterification. The present paper deals with the results of the studies carried out on preparation of linseed fatty acids-betulinol esters and their application in the field of protective coatings.

Materials

Linseed Fatty Acids.—Prepared by saponification of raw oil followed by acidification; characteristics: acid value 185, iodine value 170.

Betulinol.—Prepared from the benzene extract of *Betula utilis* (local name: Bhojputr) by double crystallisation; melting point 250-252°C.

Benzene Extract of Betula utilis.—A yellow powder; melting point 225-230°C.

Ester Gum.—Prepared by esterification of rosin with glycerol; characteristics: acid value 14-16; melting point 98-100°C.

Preparation of Esters

150 g. of linseed fatty acids and the amount of betulinol or the *Betula utilis* extract desired, were placed in a four-necked 500 ml. flask equipped with a constant speed stirrer, an inlet for carbon dioxide and a distillation connection to assist in removal of water. The flask was heated by a heating mantle regulated by a variac, and during the reaction, a gentle current of dry carbon dioxide was passed over the surface of the reaction mixture. After the desired temperature had reached, samples were removed at regular intervals for examination of acid value to evaluate the progress of reaction.

As a guide in selecting the temperature best suited for the study, tests were made at three temperatures to determine the effect of temperature on the rate of esterification. The data for these tests obtained with pure betulinol and benzene and 40/60 petroleum ether extracts are presented in Fig. 1. In all cases, the acid number reached a constant value in about 90 to 120 minutes. The preferred temperature for carrying out the esterification was 270-280°C. as against 180-210°C. required with other alcohols. It was also observed that, where extracts had been used for esterification, the acid value could not be reduced below 40. Use of excess quantity of these extracts did bring down the acid value but the film-forming properties of finished product was found to be poor. However, the use of glycerol or pentaerythritol to bring the acid value below the desired level of 20, gave satisfactory finished products.

Properties of Esters

The following properties of the esters were determined: acid value, colour value, viscosity, refractive index, density, saponification value and iodine value. The results are reported in Tables 1 and 2.

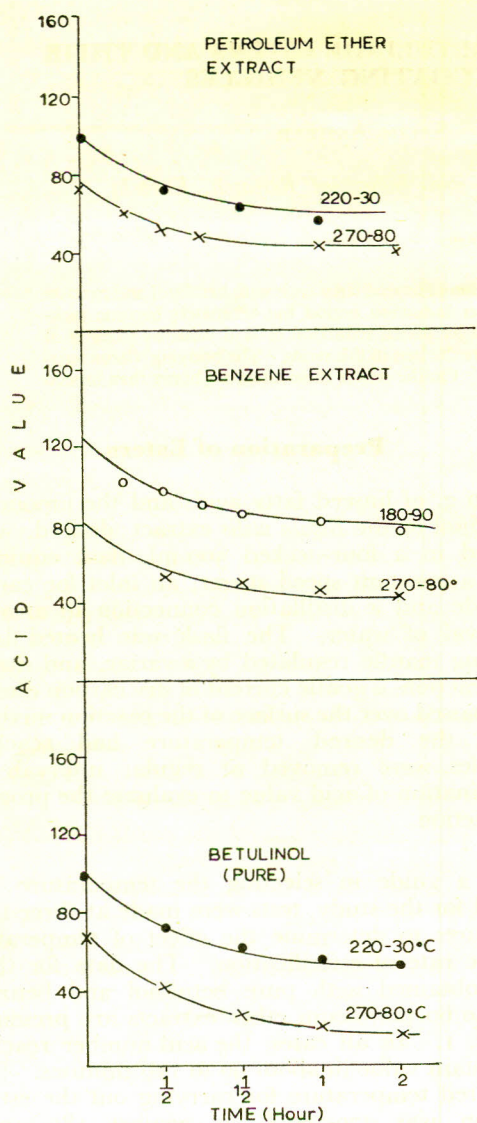


Fig. 1.—Showing esterification rate of linseed fatty acids with pure betulinol and petroleum ether extracts of *Betula utilis*.

In order to obtain reproducible iodine values, it was found necessary to control the following factors: weight of sample, 0.1 ± 0.01 g.; chloroform 20 ml.; potassium iodide (15%), 15 ml. and duration, one hour. The drying properties of these esters, determined twenty-four hours after the incorporation of driers, are reported in Table 3. The two remarkable observations are that (1) products Nos. 9 and 10 (the esters prepared by condensation of linseed fatty acids with extracts and subsequent reaction with glycerol or pentaerythritol) have excellent drying properties, and (2)

linseed-betulinol esters have a larger induction period i.e. they take more time to dry to touch but become hard-dry at about the same time as the linseed oil. Further, whereas these esters become tack-free in about 10 days, the linseed oil film still retains a slight tack. However, if the ester is heated in open at 300°C . for half an hour, induction period is greatly reduced.

The bodying characteristics of the esters was determined by heating at 300°C . for four hours. Samples were drawn every half an hour for examination of acid value, refractive index and viscosity. The results are shown in Figs. 2 and 3, from which it is evident that (1) the bodying characteristics of ester prepared from pure betulinol is the same as linseed oil whereas curve for ester prepared from the extract is linear, (2) there is a slight change in acid values in the case of betulinol based esters whereas the acid value of linseed oil shows a substantial rise with the period of cooking, and (3) the rate of increase of refractive index of betulinol esters decreases with the period of cooking whereas in the case of linseed oil, it reaches a certain maximum and then does not increase any further. The latter effect in the case of linseed oil is due to gradual increase in free fatty acids.

Preparation of Varnishes

100 g. lots of varnishes were prepared to evaluate the varnish-making qualities of the linseed fatty acids-betulinol esters, as compared with linseed oil. They were prepared by heating the ingredients at 300°C . for the desired period, cooling it to 150°C . and incorporating the thinner. Driers equivalent to 0.25% lead, 0.1% manganese, 0.01% cobalt calculated on the content were added and the varnishes allowed to mature overnight before carrying out the drying tests. No mechanical device was employed for the purpose, but the state of film was assessed by the finger at regular intervals after application. All tests were made on comparative basis. At the end of one week, the hardness of the film was determined by the scratch test.

The data in respect of various formulations and their drying properties is given in Table 4. These results show that varnishes based on the esters can become tack-free in 8-10 days even without the incorporation of driers, whereas the corresponding linseed oil varnishes are tacky even after 15 days. In general the varnishes prepared from these esters have considerably improved drying properties and became dry-to-touch in a much shorter period.

TABLE I.—BETULINOL ESTERS OF LINSEED FATTY ACIDS.

	Product number							
	1	2	3	4	5	6	7	8
<i>Reactants:</i>								
Linseed fatty acids	150	150	150	150	150	150	150	150
Betulin pure	100	—	—	—	—	—	—	—
Benzene extract	—	100	100	100	—	—	300	150
Petroleum ether extract	—	—	—	—	100	100	—	—
<i>Conditions:</i>								
Temperature °C.	270-80	270-80	270-80	180-90	270-80	220-30	270-80	270-80
Duration of heating	2	2	4	4	2	4	2	2
<i>Properties:</i>								
Acid value	16.5	43.6	40.5	67.8	40.0	43.4	10.3	17.1
Colour value	13	dark	dark	—	—	—	—	—
Viscosity (seconds)	156	—	—	—	—	—	—	—
90% solution in terpentine	—	49.5	—	—	—	—	—	—
80% " " "	3.6	9.2	—	—	3.4	1.7	—	7.4
Refractive index at 25°C.	1.5030	1.5055	—	—	—	—	—	—
Density	0.9813	0.9795	0.9880	—	—	—	—	—
Saponification value	—	130	—	—	—	—	—	—
Iodine value (Hanus)	147	145	132	—	—	—	—	—
Molecular weight	920	—	—	—	—	—	—	—

Conclusion

Linseed fatty acids can be esterified with betulinol or benzene and petroleum ether extracts of *Betula utilis* at 270-280°C. These esters take a

longer time to dry-to-touch, become hard dry in about the same time as linseed oil and become tack-free in a considerably shorter period. The induction period can however be shortened by heating the esters at 300°C. for about half an hour.

TABLE 2.—BETULINOL ESTERS OF LINSEED FATTY ACIDS.

	Product number	
	9	10
<i>Ingredients:</i>		
Product No. 2	100	100
Glycerol	5	—
Pentaerythritol	—	4
<i>Conditions:</i>		
Temperature	270	270
Duration (Hours)	1	1
Acid value	16	14

TABLE 3.—DRYING PROPERTIES OF LINSEED-BETULINOL ESTERS.

Product No.	Time (hours) taken for film to		
	Dry to touch	Hard dry	Tack free
1.	24	48	10' days
2.	30	48	10 days
7.	Crystals appear in the film		
9,10	6	24	48 hours
Linseed oil	14	48	Does not become tack-free even after 2 weeks
2 (heated at 300°C. for 30 minutes)	10	24	10 days
Driers:	Pb, 0.25%, Mn, 0.10%, Co, 0.01% added as naphthenates		

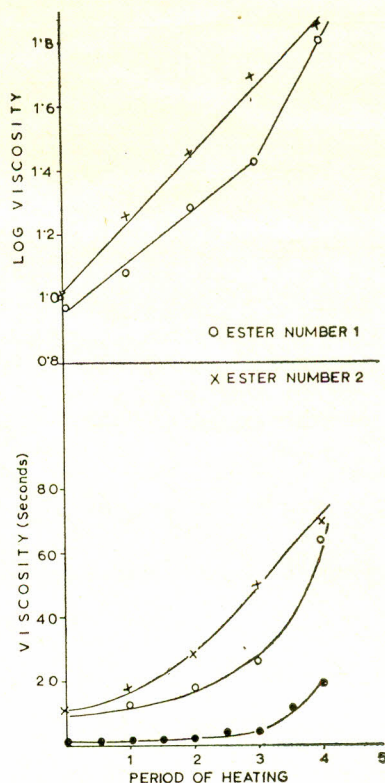


Fig. 2.—Showing polymerisation rates for (1) ●-linseed oil, (2) O-Ester No. 1, and (3) ×-Ester No. 2. Viscosity measured by bubble tube method after diluting with mineral turpentine to 80% ester content.

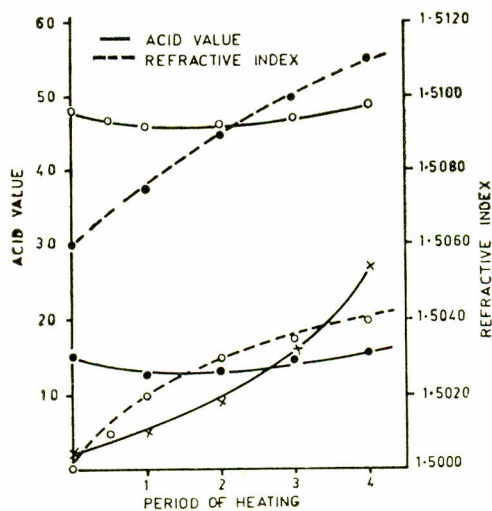


Fig. 3.—Showing influence of heating on the acid value and refractive index of (1) ×-linseed oil, (2) ●-ester No. 1, and (3) O-ester No. 2.

TABLE 4.—COMPOSITION AND DRYING PROPERTIES OF VARNISHES.

Varnish number	Ester number	Ester gum % by weight of ester	Period of cooking (hours)	Drier			Time (hours) for film to		
				Pb%	Mn%	Co%	Dry-to-touch	hard-dry	tack-free
1	2	20	0.5	0.25	0.1	0.01	2-3	24	40
2	2	50	0.5	0.25	0.1	0.01	2-3	16	30
3	2	100	0.5	0.25	0.1	0.01	2-3	6	24
4	Linseed oil	20	0.5	0.25	0.1	0.01	10-12	48	Not tack-free after one week
5	Linseed oil	50	0.5	0.25	0.1	0.01	8-10	40	72
6	2	20	1.0	0.25	0.1	0.01	2-3	16-20	30
7	2	20	2.0	0.25	0.1	0.01	1-2	10-12	24
8	2	40	2.0	nil	nil	nil	26	72	8-10 days
9	Linseed	40	2.0	nil	nil	nil	24	144	—

The bodying characteristics of the esters based on pure betulinol are similar to linseed oil but the behaviour of esters made from extracts is quite different. Furthermore, esters made by part reduction in acid value by use of extracts, followed by esterification with glycerol or pentaerythritol give greatly improved products. These esters are superior to linseed oil in respect of varnish-making qualities.

References

1. J.P. Gibbons and K.M. Gordon, *Ind. Eng. Chem.*, **142**, 1591 (1950).
2. S. Siddiqui, M. Aslam and K. Alam, *Pakistan Patent application No. 1210/63*.