PROPERTIES AND APPLICATIONS OF BETULIN-BASED ROSIN ESTERS

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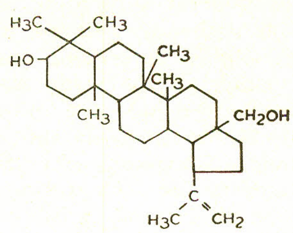
It has been observed that rosin can be esterified with betulin which is obtained by crystallisation from the extract of the bark of the *Betula utilis*, known locally as 'bhoj putr' or 'khadang'. To make the processes economically feasible, the extract as such has been successfully used for the preparation of betulin-based rosin esters. These resins are superior to ester gum in all respects and compare favourably in performance with pentaerythritol ester. The water resistance properties of varnishes based on the new esters prepared from the extract of bark as such is excellent.

Ester gum is one of the simplest of synthetic resins, being the triglyceride of rosin acids, and was originally produced to yield a material higher in melting point and lower in acid value, and therefore more satisfactory than rosin. It was first made by Schaal[1] by direct reaction of rosin with glycerol. Rosin is also esterified with many alcohols for special purposes. The alcohols used are monohydric, such as methyl and ethyl, as well as polyhydric ranging from glycols, dihydric alcohols through to glycerol and more recently (on a commercial scale) to pentaerythritol. Recent work in these laboratories has shown that betulin (betulinol) which is obtained by crystallisation from the extract of the bark of the *Betula utilis*, known locally as 'bhoj putr' and 'khadang', can be condensed with rosin to produce a new series of esters. The properties of these resins and their application in organic coatings are presented in this paper.



Betulin

1. Study of Solvents for Extraction

In order to make the preparation of betulin-based rosin esters economically feasible it is desirable to study the yield of betulin from the extracts of the bark with different solvents, and if possible, to utilize the extract as such for the reaction. A variety of solvents have been tried and the results of the yields of the extracts are given in Table 1. In case of some solvents, a portion of the extract crystallised out during extraction, in which case the less soluble matter has been separately estimated. The melting point of pure betulin is 250-252°C. From Table 1, benzene and ethyl alcohol appear to be the best solvents for our purpose.

2. Formulations Studied and their Properties

For the preparation of betulin-based rosin esters, the following different forms of the betulin starting material were tried:—

(1) Pure betulin, having a melting point of 250-52°C., 75.0% by weight of rosin.

(2) Less soluble matter of petroleum ether 80% by weight of rosin.

(3) Benzene extract, 85% by weight of rosin.

Since it was observed that the condensation of benzene extract with rosin did not lower the acid value below 40-45, further reduction in acidity was attained by adding:

(4) Lime, 2% by weight of rosin.

(5) Glycerine 4.0% by weight of rosin.

(6) Pentaerythritol 3.5% by weight of rosin.

The esterification is carried out in a 4-necked 500 ml. flask equipped with a constant speed stirrer, a thermometer, an inlet for carbon dioxide and a distillation connection to remove the water as it is formed. The reaction vessel is charged with rosin and betulin, the apparatus assembled, air flushed out with carbon dioxide and heated with a heating mantle regulated by variac. The temperature of the reaction depends on the alcohol used and is 270-280°C. for glycerol, pentaerythritol and betulin and 240-50°C. for lime. Samples are removed from time to time for acid value determination by which the progress of the reaction is followed.

The values for acid values, melting point and scratch hardness are given in Table 2, and compared with rosin, limed rosin, ester gum and pentaerythritol ester. The acid value was determined by dissolving 1-5 g. sample of the material

TABLE 1.—STUDY OF VARIOUS SOLVENTS FOR THE EXTRACTION OF *Betula utilis*.

Solvent	Less soluble matter			Completely soluble matter		
	Yield by weight of bark %	Melting point °C.	Colour	Yield by weight of bark %	Melting point °C.	Colour
Benzene	nil	—	—	30–32	235–240	light yellow
Carbon disulphide ..	13-14	252	white	7– 8	210– 20	light yellow
Carbon tetrachloride ..	12-13	220–25	white	11–12	240– 45	white
Ethyl alcohol ..	nil	nil		36–37	215–220	dark brown
Methyl ethyl ketone ..	nil	nil		32–34	210– 15	brown
Mineral turpentine ..	20–22	228–30	cream	7–8	180– 85	brown
Petroleum ether ..	19–21	245–50	white	4– 6	170– 75	yellow

TABLE 2.—CHEMICAL AND PHYSICAL CONSTANTS OF BETULIN-BASED ROSIN ESTERS.

Starting material and formulation No.	Melting point °C.	Acid value	Scratch hardness g.
Betulin ester No. 1	120— 25	15—20	190
,, No. 2	115—120	15—20	190
,, No. 3	115—120	40—45	—
,, No. 4	120— 25	16—17	220
,, No. 5	115— 20	10—12	230
,, No. 6	140— 45	10—12	250
Rosin	—	—	150
Limed rosin	—	80—85	150
Ester gum	98—100	10—12	190
Pentaerythritol ester	—	10—12	200

in about 20 ml. benzene and titrating to a phenolphthalein end point with alcoholic 0.1 N sodium hydroxide. The melting point was obtained by capillary tube method and the scratch hardness was determined as the load required for rupturing the films of these resins on a standard scratch test apparatus.

The betulin-based rosin esters, like ester gum, are easily soluble in benzene, *n*-butyl alcohol, ethyl acetate, mineral turpentine, turpentine oil and compatible with nitro-cellulose and oils but is only slightly soluble in acetone and petroleum-ether. Test panels for the water resistance tests were prepared by flowing 50% solution of resins in a solvent on to the tin panel and allowing it to dry for 48 hours. The panels were then immersed in distilled water for one week, during which period the appearance of physical defects was observed. The results are reported in Table 3.

3. Film forming Properties

Following the compatibility experiments, a linseed varnish having on oil length of 12½ gallons (oil length signifies gallons of oil per 100 lbs. of rosin) was selected for studies in film formation and equivalent standards were prepared using limed rosin, ester gum and pentaerythritol ester.

In making the linseed oil varnish, the ester (200 g.) and oil (200 g.) are charged together into an open beaker and heated to 290°C. The cooking temperature is maintained at 290°-300°C. and samples are drawn every half an hour to determine the polymerisation rate of the varnish. For this the varnishes are adjusted to a solids content of

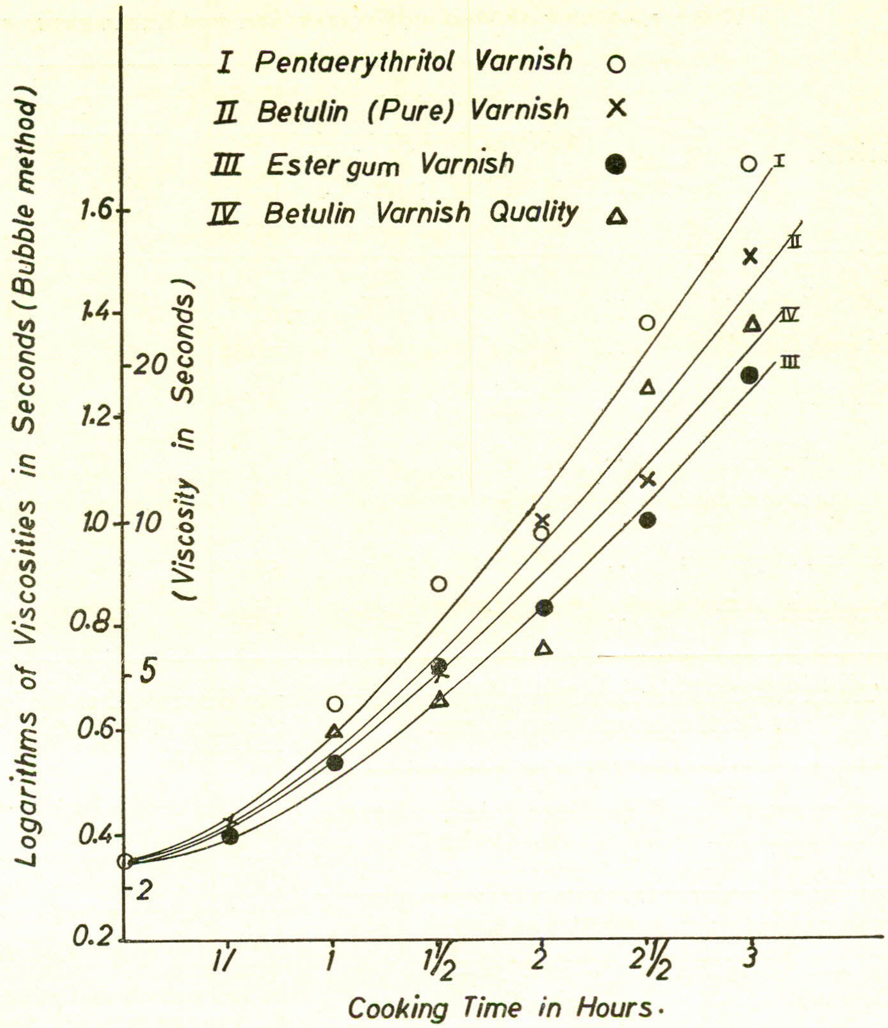


Fig. 1.—Graph showing polymerisation rates of varnishes.

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

Material under test	Blushing after immersion in cold water for				4 hours after removal from water
	4 hrs.	24 hrs.	72 hrs.	1 wk.	
Betulin esters ..	none	slight	slight to moderate	moderate	blush disappears
Pentaerythritol ester	none	slight	slight to moderate	moderate	blush disappears
Ester gum ..	none	slight	moderate	moderate to severe	blush does not disappear
Limed rosin ..	none	slight to moderate	moderate to severe	severe	film peels off
Rosin ..	slight	severe (cracks appear)			

TABLE 6.—SCRATCH HARDNESS AND WATER-RESISTANCE PROPERTIES OF VARNISHES

Material	Scratch hardness	Blushing after immersion in cold water for			4 hours after removal from water
		1 day	3 days	1 wk.	
Betulin ester No. 1 ..	750	very slight	moderate	severe	slight blushing persists
Betulin ester No. 4 ..	700	very slight	slight	moderate	blushing disappears
Betulin ester No. 5 ..	700	very slight	slight	moderate	blushing disappears
Ester gum	650	very slight	moderate	severe	remains milky
Pentaerythritol ester ..	950	very slight	moderate	severe	slight blushing persists

66.6% and the viscosity at 25°C., determined by the bubble tube method. These results are shown in Fig. 1. The drying properties of these varnishes at different stages have been determined by observing the condition of the film on a tin panel after 24 hours of application. The results are shown in Table 4. The state of film has been assessed by touch, and reported as very tacky (VT), tacky(T), hard(H) and tack-free (F). The quantity of driers used is 0.1% Pb and 0.01% Mn by weight of oil.

TABLE 4.—DRYING PROPERTIES OF VARNISHES.

Material	Drying properties after (cooking period)					
	½ hr.	1 hr.	1½ hr.	2 hr.	2½ hr.	3 hr.
Betulin ester ,, No. 1	VT	T	T	T	H	H
,, No. 4	VT	T	T	T	T	T
,, No. 5	VT	T	T	T	H	H
Pentaerythritol	T	T	H	H	H	TF
Ester gum	VT	T	T	T	H	H

The quantities of driers were increased in two instalments and their effect on drying time of the final varnishes to dry to touch (TD) hard dry (HD) and become tack-free (TF) are reported in Table 5.

Scratch hardness and water-resistance tests for varnishes are reported in Table 6, the water-resistance being determined after ageing the panels for seven days.

TABLE 5.—EFFECT OF INCREASED DRIER CONTENT ON DRYING PROPERTIES.

Material	% Pb 0.1 % Mn 0.015			% Pb 0.1 % Mn 0.020		
	T.D. min.	H.D. hr.	T.F. hr.	T.D. min.	H.D. hr.	T.F. hr.
Betulin ester No. 1	15	4-5	56	10	4-5	30-36
Betulin ester No. 4	40	24	56	30	6-8	30-36
Betulin ester No. 5	30	24	36	30	6-8	32-34
Ester gum	15	4-5	48	10	4-5	30-36
Pentaerythritol ester	15	4-5	30-36	10	4-5	24

4. Conclusion

It has been found possible to prepare betulin-based rosin esters which are superior to ester gum in all respects. The scratch hardness values of these new resins are low in comparison with pentaerythritol ester, but this property is not very important for application in coatings, while in respect of other properties these new resins give comparable results. The polymerisation rates are intermediate between those of ester gum and the pentaerythritol ester. Perhaps the most interesting part of the results is the excellent water-resistance porperties of varnishes based on the new esters prepared from the extract of the bark as such. On the other hand, these varnishes dry slowly but this can be corrected by using a slightly greater quantity of driers.

References

1. Schaal, U. S. patent 335,485 (1886).
2. S. Siddiqui, M. Aslam, Khurshid Alam, Pakistan patent application No. 824/60 (September 27, 1960).