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SYNTHETIC DRYING OIL

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Betulinol constitutes 25-28% of the bark of the *Betula utilis* (Bhojputr) found in the northern parts of Pakistan.

Esterification of betulinol with fatty acids derived from cottonseed oil, practically a nondrying oil, resulted in esters which on further bodying at 300-10° for 1/2 hr exhibited improved drying character comparable with linseed oil.

Comparative study of these esters and linseed oil in drying coating formulations is presented in this paper.

Key words. Synthetic drying oil, Betulinol, Polyhydric alcohols, Esterification.

Introduction

Drying oil fatty acids may be esterified with various polyhydric alcohols. Interesting and useful drying oils have been reported. The esters so formed are generally referred to as synthetic drying oils. The polyhydric alcohols included pentaerythritol [1-3], polypentaerythritol [4], mannitol [5], sorbitol [6] and inositol [7] whereas the fatty acids used were derived from linseed oil. We have described in a previous publication [8] that betulinol, a triterpene alcohol possessing two reactive hydroxyl groups, can be esterified with linseed fatty acids to yield protective coatings. Era and jaask-elainen [9] condensed betulinol with tall oil fatty acids and evaluated their film forming properties at ambient and elevated temperatures. Preliminary results identifying improvement in drying characteristics of esters prepared by condensation of betulinol and fatty acids of cottonseed oil, practically a non-drying oil, have been reported [10]. The present work is an extension and deals with further preparatory studies and improvements to the drying character which approach that of a drying oil.

Experimental

Benzene extract of *Betula utilis* is an off-white powder, mp, 225-30°, which on recrystallisation from ethanol gave betulinol, mp, 250-52°. Benzene extract was used in the present study without further purification. Cottonseed fatty acids were prepared by the saponification of raw oil followed by acidification, acid value 188, iodine value 105.7. Ester gum was prepared by esterification of rosin with glycerol, acid value 14.5, softening point 80° (ring and ball).

Preparation of esters. A description of the method for preparing betulinol linseed fatty acid esters has already been given [8]. The same experimental conditions were found to be suitable for the preparation of betulinol cottonseed fatty acid esters. The reaction scheme for the formation of esters under varying experimental conditions and their physico-chemical properties are illustrated in Table 1. Ester 3 (acid value II) was

partially freed of unreacted fatty acids by subsequent distillation under reduced pressure of 15 cm of Hg at 150°. The esterification rate was assessed by removing samples periodically. These were cooled and titrated for their acid value. Fig. 1 compares the esterification rate at varying temperatures. Various catalysts generally used in esterification reactions including zinc oxide, zinc powder, aluminium chloride and p-toluene sulphonic acid were employed at lower reaction temperatures. It was found that in the esterification of betulinol and cottonseed fatty acids, the primary factor is the degree of heating and not the catalyst. The reaction rate conducted at 270-80° diminished at about acid value 50. The acidity of esters, however, was subsequently reduced to desired level by esterification with glycerol and pentaerythritol. Use of an excess quantity of extract resulted in the formation of product of low acidity with poor film properties. Drying properties of these esters and their varnishes are compared with those of linseed oil in Table 2.

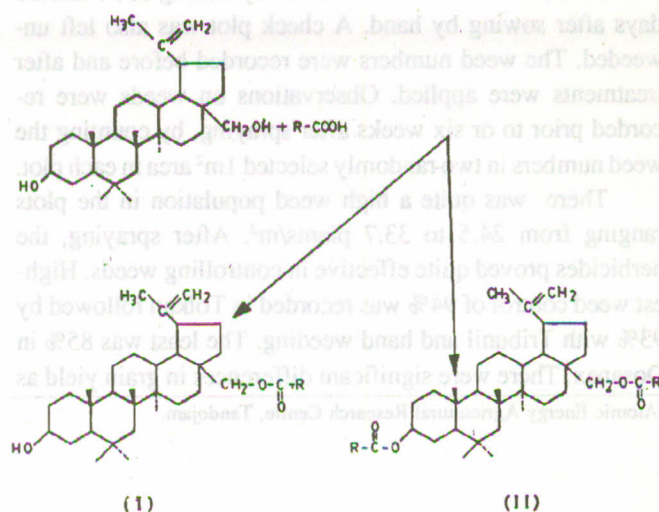


Fig. 1. Esterification of betulinol-cottonseed acids

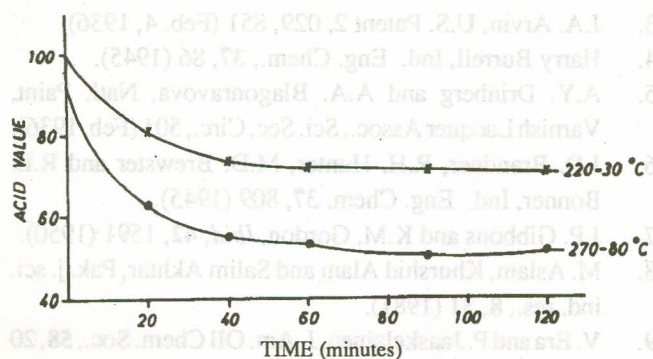


Fig. 2. Esterification of betulinol- cottonseed acids

Results

Properties of esters. Table 1 compares data on physical and chemical constants of these esters. The esterification is expected to result in the formation of a mixture of mono- (I) and di-esters (II) of betulinol owing to different reactivities of primary and secondary hydroxyl groups. All esters were of considerable high body with colours slight darker than that of cottonseed oil or of the acids used. The drying properties were assessed by incorporating the drier combinations reported in Table 2. The film were cast 24 hr after the addition of driers. The ester showed an average touch-dry period of about 50 hr. The period was reduced to half if the esters are cooked at 300-10° prior to addition of driers. The drying behaviour of linseed and cottonseed oil under identical conditions also compared, the former took 18-20 hr to dry-to-touch while the latter showed no tendency to dry even after two weeks.

Preparation and comparison of surface coatings. Varnishes of betulinol cottonseed acids were prepared in batches of 100 g in open round-bottomed flasks heated in a high boiling oil bath. After the varnish had been cooked, it was allowed to cool followed by thinning to 50% solids with mineral spirit. Naphthenates equivalent to 0.5% lead, 0.2% manganese and 0.02% cobalt on the basis of ester were added 24 hr before the films were formed. For comparative purposes, linseed and cottonseed oils were also cooked into varnishes. Film were tested for their drying period by finger touch at regular intervals after application. Scratch resistance was determined by 'Sheen' hardness tester.

The results reported in Table 2 show that the varnish based on ester I has a considerably reduced induction period compared to linseed oil, however, the reverse is true for a tack-free state. Ester 4 varnish compares favourably with linseed oil whereas the ester 5 based composition led in respect of drying

TABLE 1. PHYSICO-CHEMICAL PROPERTIES OF BETULINOL COTTONSEED FATTY ACIDS ESTERS.

Ester no.	1	2	3	4	5
Acid value	51.3	48.7	11.0	19.2	12.3
Saponification value	—	—	—	1119.5	120.2
Iodine value	108.1	107.3	106.2	106.5	111.0
Refractive index	1.492	1.493	1.492	—	—
Density, 30°	0.972	0.978	0.968	0.981	0.985

Betulinol - fatty acids ratio, 1:1.5; temperature, 270-80°; heating period: ester 1 and 3, 2 hr; ester 2, 5 hr; ester 4 and 5, 3 hr. Ester 4 and 5 further esterified with glycerol and pentaerythritol respectively.

TABLE 2. DRYING PROPERTIES OF ESTERS AND VARNISHES.

	Cooking period	Drier (naphthenates)			Time (hr) for the film to		Scratch hardness
		Pb%	Mn%	Co%	touch-dry	tack-free	
Ester 1	—	0.25	0.1	0.01	60	—	—
Ester 1	—	0.50	0.2	0.02	55	—	—
Ester 3	—	0.25	0.1	0.01	40-45	—	—
Ester 4	—	0.5	0.2	0.02	50-55	—	—
Ester 5	—	0.5	0.2	0.02	45-50	—	—
Ester 1	2	0.25	0.1	0.01	24-26	—	—
Ester 1	4	0.25	0.1	0.01	24-26	—	—
Ester 4	2	0.5	0.2	0.02	22-24	—	—
Ester 5	4	0.5	0.2	0.02	22-24	—	—
Cottonseed oil	2	0.5	0.2	0.02	No tendency to dry at all		—
Linseed oil	2	0.5	0.2	0.02	18-20	—	—
Ester 1 varnish	2	0.5	0.2	0.02	5-6	70	500-550
Ester 3 varnish	2	0.5	0.2	0.02	3	12	500-550
Ester 4 varnish	2	0.5	0.2	0.02	4-5	40	550-600
Ester 5 varnish	2	0.5	0.2	0.02	3-4	16	700-750
Linseed oil varnish	2	0.5	0.2	0.02	8-10	40	600-650
Cottonseed oil varnish	2	0.5	0.2	0.02	No tendency to dry		—

Varnish formulations : 40% of ester gum by weight of betulinol-cottonseed fatty acids ester.

and scratch hardness. Varnish prepared from ester 3 (acid value reduced by distillation of free fatty acids) exceeded esters in drying character whose acidity was reduced by glycerol or pentaerythritol. However, this improvement is accompanied by a slight decrease in scratch hardness. The drying characteristics of these esters appeared to be least dependent on oil length and prolonged cooking period of varnishes.

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