Esters of Rosin and Olefin Epoxides

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Abstract

Rosin has been found to react extremely rapidly with commercially available olefin 1,2-epoxides to give hydroxy monoesters. These monoesters have been reacted further with rosin to give diesters. The diesters are ester gums, which are modified by the presence of a long aliphatic chain in the molecule. Preliminary results indicate that they are useful as tackifiers for SBR rubber.

Introduction

THE COMMERCIAL AVAILABILITY of olefin 1,2-epoxides (Nedox 1114 and Nedox 1518) made it seem desirable to react these long-chain epoxides with rosin. The products were believed to be potentially useful in many areas in which ester gums are now used. The presence of the long aliphatic chain should modify the physical properties of the products to a considerable extent.

Experimental Procedures

The monoester was prepared as follows. Gum rosin (USDA rosin color grade of WW; acid number 165, hydroxyl number 24, saponification number 178) (954 g) and calcium hydroxide (9.54 g) were heated to 210C under a sweep of nitrogen to remove the water which was formed; and 742 g of Nedox 1518 (oxirane number 212) (1 mole carboxyl/1 mole epoxide) were added. The temperature was held at 190C under nitrogen for 15 min, at which time the acid number was zero. The product exhibited a USDA rosin color grade of K, hydroxyl number of 109, saponification number of 86, and a Gardner bubble viscosity of Z-4. Some isomerization of the rosin acids to abietic was indicated by the increase in α from 32 (starting rosin) to 41 at λ 242 mμ (based on rosin acid content). The infrared spectrum exhibited $\lambda_{\max}^{\text{neat}}$ 2.94 μ (s) (hydroxyl), 5.80 μ (s) (ester), and no absorption for carboxyl. The monoester was soluble in acetone, alcohol, ethyl acetate, ether, benzene, iso-octane, chloroform, and petroleum ether; it was insoluble in water and acetonitrile. The catalyst was removed by washing a portion with 1 *N* hydrochloric acid in ether solution and water-rinsing. The properties of the catalyst-free material are listed in Table I.

The diester was prepared by adding 388 g of WW gum rosin to 688 g (1 mole hydroxyl/1 mole carboxyl) of the monoester, in which the catalyst still remained. The mixture was blanketed with nitrogen and heated at 240–245C for 11 hr with stirring. At the end of this period the acid number had dropped to 4.0. The observed $\lambda_{\max}^{\text{EtOH}}$ 241 mμ (α 49.0) (based on the resin acids present) showed that some further isomerization had occurred during reaction. The catalyst was removed by washing with acid. The properties of the product are given in Table I.

An ethylene oxide adduct of the monoester was prepared as follows. The monoester was prepared, as above by using 1% on the weight of the rosin of potassium hydroxide as catalyst. The ester with catalyst was heated to 180C, and ethylene oxide was passed through the solution. Unreacted ethylene oxide was trapped in an ice-cooled trap and recirculated through the system. After 2.5 hr 10 moles of ethylene oxide per mole of monoester had reacted with the hydroxyl group. A 100-g sample was dissolved in ether; washed with 1 *N* hydrochloric acid, saturated with sodium sulfate, to remove the catalyst; then washed to neutrality with water which was saturated with sodium sulfate. The ether was removed to give 92 g of product of acid number 4.2, Gardner bubble viscosity of U, USDA rosin color grade of M. It was soluble in water and acetonitrile. The wetting time in a standard Drave's test was 75 sec for 0.50% concentration of 77F. In comparison, a 0.50% concentration of potassium oleate gave a wetting time of 40 sec. Ten more moles of ethylene oxide/mole of monoester were added to the ethylene ooxide adduct. The wetting power of the product was decreased.

TABLE I

Preparation of Esters of Rosin and Olefin 1,2-Epoxides

			Properties of Product [a]					
Rosin	Epoxide	Product	USDA rosin color grade	Acid No.	Hydroxyl No.	Saponification No.	Gardner bubble viscometer	Ball and ring softening point, °C
Gum rosin	Nedox 1518	Monoester	WW	4.5	111	103	Z-4	....
Gum rosin	Nedox 1114	Monoester	WW	5.4	122	112	Z-3	....
Disproportionated rosin [b]	Nedox 1114	Monoester	WW	4.8	119	104	Z-3	....
Gum rosin	Nedox 1518	Diester	WG	5.5	20	......	......	34.0
Gum rosin	Nedox 1114	Diester	*WG*	4.4	24	... ..	......	36.5
Disproportionated rosin [b]	Nedox 114	Diester	*WG*	5.4	19	......	......	38.5

[a] Catalyst removed by acid wash.

[b] Acid number 162, hylroxyl number 26, saponification number 183.

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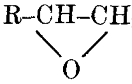
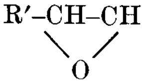
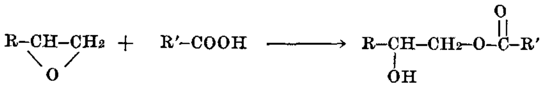
Nedox 1114 can be represented by the formula  $\underset{\diagdown\,O\,\diagup}{R{-}CH{-}CH_2}$ where R– is a saturated straight chain containing 9 to 12 carbon atoms. Nedox 1518 can be written  $\underset{\diagdown\,O\,\diagup}{R'{-}CH{-}CH_2}$ where R′– is a saturated straight chain containing 13 to 16 carbon atoms.

The reaction of these two fatty olefin 1,2-epoxides with the carboxyl group in rosin in the presence of a basic catalyst, such as calcium oxide or potassium hydroxide, proceeds as fast as or faster than any organic reaction of the rosin carboxyl group known to the authors. Acid numbers of zero are regularly obtained in less than 10 min of heating at 190 and 200C. In the absence of a basic catalyst the reaction is much slower, and some diester is formed. The presumed structure of the reaction product of one mole of the epoxide and one mole of rosin as is follows.

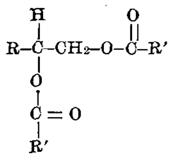


$$\underset{\diagdown\,O\,\diagup}{R{-}CH{-}CH_2} + R'{-}COOH \longrightarrow R{-}\underset{OH}{CH}{-}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'$$

where R′ is the rosin moiety and R is the saturated straight chain.

Reaction of the monoester with ethylene oxide at atmospheric pressure in the presence of potassium hydroxide as a catalyst occurs readily. The product containing 10 equivalents of ethylene oxide exhibits a wetting power in the neighborhood of that demonstrated by potassium oleate.

Reaction of the monoester with a second mole of rosin is carried out without removing the basic catalyst from the preparation of the monoester. The reaction proceeds readily in the temperature range of 240C. The structure of the diester can be written as follows:



where R′ = rosin acid moiety and R is the straight saturated chain. It can be seen that the diester is a glycol ester gum of rosin, modified by the presence of a long aliphatic chain. This should give this "modified ester gum" some unusual properties. The hydroxy monoesters are liquids, but the diesters are solids with a ball and ring softening point of 34–38.5C. In comparison, the ball and ring softening point of an ethylene glycol diester of abietic acid is about 65C (1). Preliminary tests indicate that the monoester and the diester are as effective as a commercially used tackifier for SBR-1006 rubber formulations at moderate contact times (15 min) but superior to a commercial product at short contact times (0.5–5 min) (2). The diester is superior to a commercially used tackifier at a 30-minute contact time.

REFERENCES

1. Buttrey, D. H., "Plasticizers," Interscience Publishers Inc., New York, 1950, p. 94.
2. Berry, David, Battelle Memorial Institute, unpublished results.

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