

# Esters of Rosin Acids and Glycidyl Ethers

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## Abstract

Rosin and hydroxymethyl derivatives of rosin acids react rapidly with commercially available glycidyl ethers to give the hydroxy monoesters of aliphatic ethers. These esters of rosin, oxonated rosin and tetrahydroabietic acid are viscous liquids of low acid number and high hydroxyl number with a light to golden amber color. In the case of 12-hydroxymethyltetrahydroabietic acid, the products are colorless gums of a tacky, semisolid consistency. The acid, hydroxyl and saponification values, and the viscosities and softening points are tabulated.

## Introduction

An ongoing project in this laboratory is the commercial utilization of gum rosin and derivatives therefrom in the areas of condensation polymers, polyurethanes, adhesives, tackifiers, etc. In these applications the more potentially useful products of rosin are the hydroxy esters, in particular the polyhydroxy derivatives for use in polyurethane compositions presently being studied. Esterifications of rosin acids with monohydric alcohols or glycols in the usual manner require such high temperatures and long reaction times that much diester or, as in the case of the methylolated acids, considerable polyester is formed, due to intermolecular condensation. Olefin epoxides have been shown to be extremely reactive esterifying agents for the tertiary carboxyl of rosin acids and provide the hydroxy monoesters in high yield (1,2).

The commercial availability of long-chain glycidyl ethers (P & G Epoxides No. 7 and 45) suggested that they would provide interesting hydroxy esters, as the long-chain aliphatic ether groups should favorably modify the physical properties of the products for utilization in the above mentioned areas where lower softening points and viscosities are desirable. This would apply particularly to utilization of the polyhydroxy derivatives as extenders in urethane foams. Recent work has shown that the use of alkoxy derivatives of rosin products as extenders produced rigid foams of enhanced properties at lower costs (3). The percentage amount of rosin extender was limited due to the high viscosity of such solutions. Such derivatives as reported here with their lower viscosity and softening points could

conceivably allow a higher percentage of resin to be used.

The glycidyl ethers used can be represented by the general formula  $R-O-CH_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-CH_2$  in which

the alkyl group R is predominantly *n*-octyl and *n*-decyl for Epoxide No. 7; for Epoxide No. 45 the alkyl groups are largely *n*-hexadecyl and *n*-octadecyl. A GLPC of both epoxides showed two major peaks of the glycidyl ethers and minor peaks for the presence of lower molecular weight material. The oxirane oxygen content, 6.3–7% for No. 7 and 3.7–4.3% for No. 45, also indicated the presence of some material other than epoxides; accordingly, the average molecular weight, or equivalent weight, of the two epoxides was calculated on the basis of the oxirane oxygen content to react with the rosin acids on a mole to mole basis. The neutral equivalent values for rosin and rosin derivatives were used as the average molecular weight of the acids.

Oxonated rosin, the product from reacting rosin with carbon monoxide and hydrogen using a cobalt catalyst (4), is a completely hydrogenated mixture of mono- and di-hydroxymethylated rosin acids and hydrogenated unreacted rosin acids. The oxonated rosin esters were viscous liquids of light to golden amber color as were the esters of the saturated tetrahydroabietic acid. The less viscous esters derived from gum rosin (color grade WW) were a dark amber color.

The 12-hydroxymethyltetrahydroabietic acid [12-HMTHAA] (5) used was a crystalline material of good purity (mp 232–235 C). The esters produced in both cases were colorless gums of a tacky, semisolid consistency. The esters of Epoxide No. 7 were tacky even at –20 C (as were the No. 7 esters of oxonated rosin); the product with Epoxide No. 45 was tack-free at this low temperature. The physical properties of the glycidyl ether esters are shown in Table I.

The hydroxyl and saponification values found indicate that the monoester was the principal product formed with the epoxide. The complex mixture of the oxonated rosin material, mono- and di-hydroxymethyl acids along with polyesters produced in the oxo process, would make an accurate, meaningful analysis of the esterification reaction very difficult and it was felt beyond the scope of this investigation. In the case of the esters formed with tetrahydroabietic

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TABLE I  
Preparation and Properties of Glycidyl Ether Esters

Resin acids	No. Epoxide	Acid No.	Hydroxyl No.	Saponification No.	Gardner bubble viscometer	Ball & Ring softening point, C	Color
Gum rosin (NE 343)	7	6.1	124	120	Z-4	....	Dark amber
	45	11	99	93	Z-2	....	Dark amber
Oxonated gum rosin (NE 462; OH No. 104)	7	8.6	149	114	>>Z-6	5	Light amber
	45	7.7	127	94	>Z-6	20	Light amber
Oxonated wood rosin (NE 423; OH No. 132)	7	11.5	146	109	>>Z-6	2	Light amber
	45	8.8	127	90	Z-6	20.5	Light amber
12-Hydroxymethyltetrahydroabietic acid (NE 341)	7	22.4	133	92	....	4	White
	45	31.7	144	62	....	25.5	White
Tetrahydroabietic (NE 303)	7	10.6	108	109	V	....	Golden amber
	45	4.8	94	93	X	....	Golden amber

acid of good purity, the close agreement between the hydroxyl and saponification numbers shows very little formation of diester. The saponification numbers of the gum rosin and oxonated rosin correlate well with those of the tetrahydroabietates. While the esters made of 12-HMTHAA have hydroxyl values that are in good agreement for the dihydroxy monoesters, the saponification number for the No. 45 ester (adjusted for acid value) is much too low. It is also to be noted that the acid numbers of those two ester products were quite high. No satisfactory explanation of this variance from the other products was found.

### Experimental Procedures

The esters were prepared, in general, as follows. Oxonated gum rosin (NE 462, OH No. 104), 46 g and 0.46 g  $\text{Ca}(\text{OH})_2$  were heated to 185 C under sweep of  $\text{N}_2$  to remove water and 37 g (0.1 mole epoxide) of Epoxide No. 45 was added. The temperature was kept at 185–190 C for 45 min at which time the acid number was 0.7. The cooled product was taken up in ether and washed with 1 N hydrochloric acid to remove the catalyst, followed by

washing with water and saturated salt water. Table I lists the properties of the catalyst-free products. Infrared spectra of all products showed absorption at  $3.0\mu$  (OH) and  $5.85\mu$  (ester) and no absorption for carboxyl.

The softening points of the esters were determined by the ASTM ball and ring method used for rosin. Rings filled with ester were cooled to 20 C and softening points were determined in a salt-ice water bath starting at  $-4$  C.

The saponification numbers were determined by the method of Johnson and Lawrence (6) and the hydroxyl numbers were determined by the acetic anhydridypyridine method of Sorenson (7).

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