

New Resinous Ricinoleic Polyol for Urethane Reactions

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ABSTRACT

A new resinous polyol has been described based on a fusion reaction of Epon Resin 829 with Bisphenol A and further esterification with ricinoleic acid. This was based on a modified short oil alkyd cook reaction with unsaturated fatty acids following previously employed techniques. The method was modified by reaction with ricinoleic acid, a 12-hydroxy oleic acid, the main fatty acid component of castor oil. The resinous polyol derived from this technology is designated Ester 597. Ester 597 was further reacted with a series of urethane prepolymers based on castor oil. A two-component formula based on this study was used to prepare a two-can epoxy-urethane coating system that may have coatings potential as a marine coating and as a maintenance coating for industrial use.

INTRODUCTION

This investigation was part of our overall combined research, technical service, and developmental programs to develop new markets for our P-10 acids, or ricinoleic acid. Ricinoleic acid chemically is 12-hydroxy oleic acid. It is derived from the seed of the castor plant, *Ricinus communis*, from which its name is derived. Castor oil contains about 90% ricinoleic acid. Ricinoleic acid is the main hydroxylated fatty acid derived from plant sources and of commercial significance. We had been previously employing ricinoleate esters of castor oil as polyols in two-can urethane casting products for potting and encapsulating systems. These systems were noted for their shock resistance, and good electrical properties and low shrinkage values. On the other hand, epoxy resin finishes are known to be hard and brittle finishes. The possibility of combining these properties to develop a plasticized epoxy-urethane system based on ricinoleic acid was the basis of this study.

EXPERIMENTAL PROCEDURES

Materials and Methods

We screened some of the "Epon" resins of Shell, the "Araldite" resins of Ciba, and the Dow resins. It was determined that a standard epoxy resin of around 1000 molecu-

lar weight was useful. This resin was reacted in a standard L-4 type cook which is used with "9,11 Acids" to develop short oil type alkyds for use in can linings (1). We modified this procedure by reacting a commercial resin such as Epon Resin 1004 with ricinoleic acid in this type of alkyd cook. The operations presented some problems since the resin was a solid, and the end product exhibited very high viscosity levels, which made it difficult to handle. We then took a liquid epoxy resin of lower molecular weight, such as Epon Resin 829. This resin is a 96.5% solution in xylene. We extended this resin in situ with Bisphenol A following recommended fusion procedures. The extended resin was further reacted with ricinoleic acid following standard procedures employed for other dryer type polyunsaturated fatty acids. The end product was then thinned with xylene to 50% solids to a Z-1 viscosity by the Gardner bubble method. This product was designated Ester 597, a ricinoleic resinous polyol. Ester 597 polyol was reacted further with our "VORITE" line of urethane prepolymers to screen and develop a new epoxy-urethane for coating applications. Several of the VORITEs were screened, and we settled on VORITE 128 and VORITE 144 for further detailed studies. These studies included the optimum selection of catalyst and catalyst levels, as well as variations of the hydroxyl/isocyanate ratios for the system studied.

The method for the preparation of Ester 597 is outlined in three stages.

First stage or fusion reaction: 412 g of Epon 829 (equivalent wt 195.3, 2.11 moles epoxy) and 174 g of Bisphenol A (molecular wt 228, .763 moles) are charged to a 2,000 ml resin flask setup with a Dean-Stark trap. The mixture is stirred and heated to 135-145 C. The reaction then exotherms to 155 C, when the exotherm subsides. The fusion reaction is completed by stirring the molten mass at 175-180 C for 1/2 hr.

Second stage or esterification reaction: To the fused molten resin solution is added 393 g P-10 Acids (ricinoleic acid) (molecular wt 298, 1.32 moles), 0.30 g of sodium carbonate, and 14 g of xylene. The reaction is run at 255-260 C, and the xylene carried over any water of reaction. Intermittent samples are collected and diluted 1:1 with xylene and checked for acid value. The reaction was about 3-5 hr, or until a minimum acid value of about 1-2 is attained.

Third stage or dilution: The esterified solution is cooled to 145-150 C. Then 874 g of xylene are added with stirring and cooling. The batch should be a clear solution at room temperature. A final trace of haze in the liquid may require a pressure filtration through a filter pad for clarification of the end product.

Ester 597 was evaluated with various VORITE urethane prepolymers in an attempt to develop and evaluate an epoxy-urethane two-can coating system.

TABLE I

Epon 829 Properties

% Nonvolatiles	96.5
Gardner color	2
Gardner, Holdt viscosity, 25 C	Z2
Equivalents epoxide	0.512 equiv./100 g
MW Calculated	390

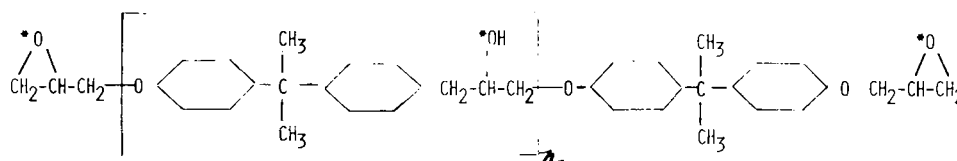


FIG. 1. Epoxy resin based on reaction of Bisphenol A with epichlorohydrin. Sites for reaction with fatty acid.

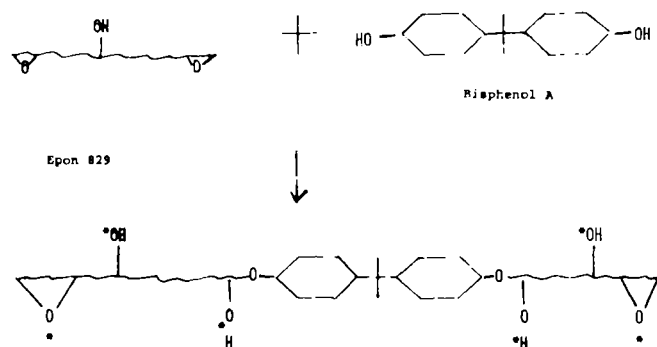


FIG. 2. Preparation of Ester 597, stage 1. Fusion reaction: postulated in situ development of extended resin by reaction of Epon 829 with Bisphenol A. Sites for reaction with fatty acid.

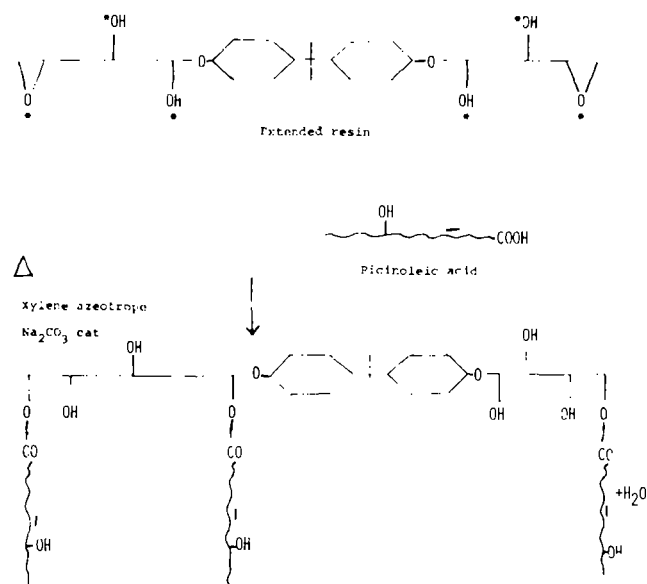


FIG. 3. Preparation of Ester 597, stage 2. Esterification with ricinoleic acid. Sites for reaction.

RESULTS AND DISCUSSION

Preliminary products were developed by reacting typical epoxy resins of 1000 molecular weight with ricinoleic acid. A typical epoxy resin based on the reaction of Bisphenol A with epichlorohydrin is depicted in Figure 1. The three potential sites for reaction with fatty acid are indicated by the asterisks. In practice, we found it more feasible and economical to react a lower molecular weight liquid resin (Shell's "Epon 829") with Bisphenol A in a fusion reaction to develop an in situ resin solution for further reaction with ricinoleic acid. The properties on Epon 829 are given in Table I. The properties as given have been used to calculate a resin molecular weight of 390, if we consider a resin of two terminal epoxy rings. In Figure 2 we have postulated a reaction route for this further extension of the liquid resin

TABLE II

Ester 597 Specifications

Gardner color	4-8
Acid value	1-3
Gardner, Holdt viscosity, 25 C	Z2 to Z3
Hydroxyl value	60-70
% Volatiles	47-54
% Water (K.F.)	.05-0.1
Specific gravity, 25 C	0.965-0.973
Viscosity, cps, 25 C	4,000
Hydroxyl equivalent wt	837

TABLE III

Properties of Urethane Prepolymers

	VORITE 128	VORITE 144
Chemical type	Ricinoleate prepolymer	Trimethylolpropane-TDI adduct
% Nonvolatile	100	75
Solvent	None	Ethyl acetate
Gardner color	2	2
Viscosity, poise, 25 C	215	30
% NCO	10.8	12.0
Equivalent wt	388	350
Specific gravity, 25 C	1.077	1.180
Pour point, °F	35	—

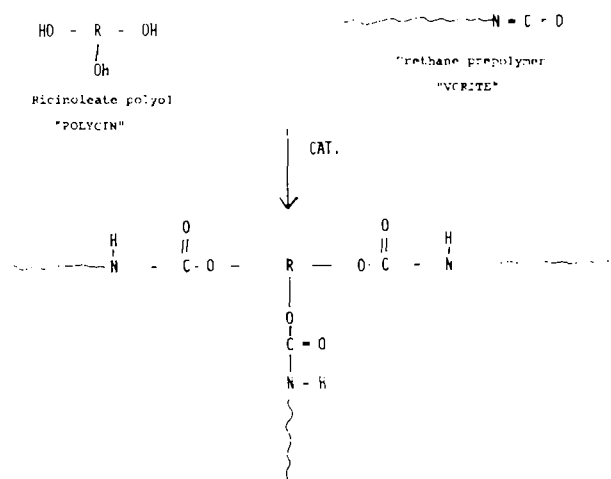


FIG. 4. Two-can urethane system. Catalyzed reaction of ricinoleate polyols (POLYCIN) with urethane prepolymer (VORITE) to produce cured urethane polymer.

with Bisphenol A. The reaction of this extended resin with ricinoleic acid ("P-10 Acids") is depicted in Figure 3. The epoxy ring opening reaction does not theoretically yield any by-products or water but does result in the formation of an ester linkage and another secondary hydroxyl group. These alcoholic groups will react with the hydroxy fatty acid by a standard esterification route and yield a water

TABLE IV

Properties of Ester 597/VORITE 128 System after Combining

Sample	VORITE	OH/NCO ratio	% Solids	Initial Gard. Visc.	Time, hr				
					1	2	3	4	5
55-1 ^a	128	1:1	40	G	I	N	U-V	Z7	Cured
55-2 ^b	128	1:1	40	G	J	K-L	T	Z7	Cured

^a55-1 0.2% of 8% Zn octoate.

^b55-2 0.05% or 8% Zn octoate.

TABLE V
Compositions of Comparative White Enamels at
20% Pigment Volume Concentration

Component A	Ester 597/VORITE 144		Epoxy-Polyamide	
	RA-45 ^a		Genamid 2000	
	Ester 597	240 lb, 23%	Versamid 280-B-75	20 lb, 1%
	Xylene	330 lb, 31%	Butyl alcohol	280 lb, 13%
		336 lb, 32%	RA-45 ^a	304 lb, 14%
				750 lb, 36%
Component B	VORITE 144	150 lb, 14%	Epon 815	500 lb, 24%
			Super Hi Flash Naphtha	250 lb, 12%

^a"Titanox 2015," rutile titanium dioxide.

TABLE VI
Properties of Ester 597/VORITE 144 vs. Epoxy Polyamide
20% PVC Enamel

	Ester 597/VORITE 144	Epoxy-Polyamide
Viscosity, K.U.	61	86
Hegeman Grind	7	7
Brushometer viscosity	2.4	4.2
Tack free time, hr	1	5
Gloss	93	98
Adhesion ^a , 24 hr, cross hatch		
glass	No Loss	No Loss
tin	No Loss	No Loss
steel	No Loss	No Loss
aluminum	No Loss	No Loss
Sward hardness, 1.5 mil ^b drawdown		
1 day	46.5	31.5
4 days	48.5	49.5
Sward hardness, 3.0 mil ^c drawdown		
1 day	39.5	19.5
4 days	48.5	42
Impact, direct	pass 160 lb/in.	pass 160 lb/in.
Impact, reverse	pass 60 lb/in.	pass 160 lb/in.

^a1.75 mil dry film.

^b0.8 to 1.0 mil dry film.

^c1.75 mil dry film.

TABLE VII
Further Comparative Properties on Ester 597/VORITE 144
vs. Epoxy Polyamide Coating (20% PVS)

	Ester 597/VORITE 144	Epoxy-Polyamide
Stain resistance ^a		
Nail polish	Etched	Some etching
Lipstick	No effect	Stained
Coffee	No effect	Stained
Shoe polish	No effect	No effect
Ball point Ink	Stained	Stained
Magic marker	Stained	Stained
Flexibility, Mandrel	Pass 1/8"	Pass 1/8"
Free film	Slightly brittle	OK
Chemical resistance		
HCl, 5%	No effect	Some bubbling
HCl, 10%	No effect	Bubbling
HNO ₃ , 5%	Some Yellowing	Etched
Acetic acid, 10%	No effect	Etched
Citric acid, 10%	No effect	Some etching
Xylene	No effect	---
Toluene	No effect	---
Mineral Spirits	No effect	No effect
Super Hi Flash Naphtha	No effect	No effect
Methyl ethyl ketone	Etched	No effect
Monochloroethane	No effect	---
NaOH, 10%	No effect	No effect
Tap H ₂ O	No effect	---
Detergent	No effect	No effect
Butyl alcohol	No effect	No effect
"Butyl Cellosolve"	Etched	No effect
Butyl acetate	No effect	No effect
Isopropanol	No effect	---

^aReagents were allowed to stand overnight before observation. The proper solvent was used to remove staining materials.

molecule for each molecule of fatty acid. The properties of the ricinoleic polyol obtained, which is designated Ester 597, are given in Table II. The results are based on laboratory and pilot plant runs. This low acidity esterified polyol of low moisture content was reacted with our VORITE line of urethane prepolymers. In Figure 4, we have sketched the typical three dimensional cured urethane system based on the reaction of polyols ("POLYCIN") with the urethane prepolymer ("VORITE"). This is the basis of our two-can urethane coating systems for potting and encapsulation applications (2). Many of our prepolymers were screened for reaction with Ester 597. The best combination of can stability and curing rate was developed with VORITE 128 and VORITE 144. These were then selected for an in-depth study of a two-can epoxy urethane coating system. The properties of the two selected urethane prepolymers are given in Table III. Table IV shows the data obtained for two levels of 8% zinc octoate catalyst on a two-can system based on Ester 597/VORITE 128 based on 1:1 OH/NCO ratios. The systems were reasonably can stable 3 hr after mixing. The VORITE 128 system did not meet the expected tear strength properties for impervious coating applications. We therefore utilized a nonricinoleate prepolymer, VORITE 144, which substantially reduced the plasticization effect of the system. Figure 5 depicts a plot of viscosity versus time for the Ester 597/VORITE 144 system at three different OH/NCO levels, 1.1/1.0, 1.0/1.0, 0.9/1.0. The systems were cured with 0.2% of dibutyltin-dilaurate catalyst. The results are reasonably close; also the three systems are can stable 3 hr after mixing. We selected an OH/NCO level of 1.0:1.0 as the system for further studies.

The epoxy ester coating system was developed as a white enamel at 20% pigment-volume concentration (PVC), and the comparative results were made on a standard epoxy-polyamide formulation (3). Table V illustrates two comparative formulations. The physical properties of the two comparative coatings systems are given in Table VI. We note that after initial mixing the Ester 597 system is lower in viscosity and has a good Tack Free Time, as the dry film. The adhesion properties are equivalent as are the seeding characteristics, as given by the Hegeman Grind. The gloss is slightly better on the epoxy-polyamide system. Further comparative film properties are given in Table VI. Overall, the Ester 597 coating is harder and not as good on the Reverse Impact Test. Table VII illustrates some of the comparative staining characteristics of the two coatings to several common materials. The Ester 597 coating is better and is more resistant to coffee and lipstick stains than the epoxy-polyamide system. Some other film properties and the chemical resistance of the two coatings are summarized in Table VII. We note that the Ester 597 coating is more brittle than the polyamide system, although both passed the 1/8" Mandrel for flexibility. It is noteworthy that the Ester 597/VORITE 144 system is resistant to acids, whereas the Epoxy-Polyamide system fails in this property. Certain oxygenated solvents such as methyl ethyl ketone or "Butyl Cellosolve" affect the Ester 597 coating but do not affect the polyamide system. Most other aromatic, ester,

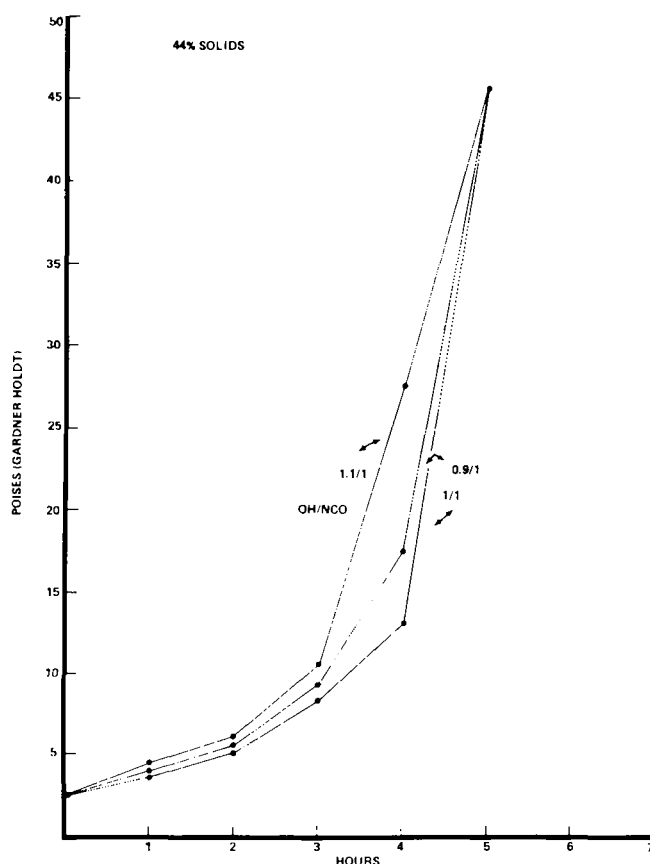


FIG. 5. Viscosity changes versus time for the Ester 597/VORITE 144 system at varying hydroxyl to isocyanate ratios.

aliphatic, or alcoholic solvents, as well as caustic, do not effect the impervious Ester 597/VORITE 144 coating.

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