

## Vinyl Oil Monomers. I. Vicinal Methacryloxy-Hydroxy Soy Oils

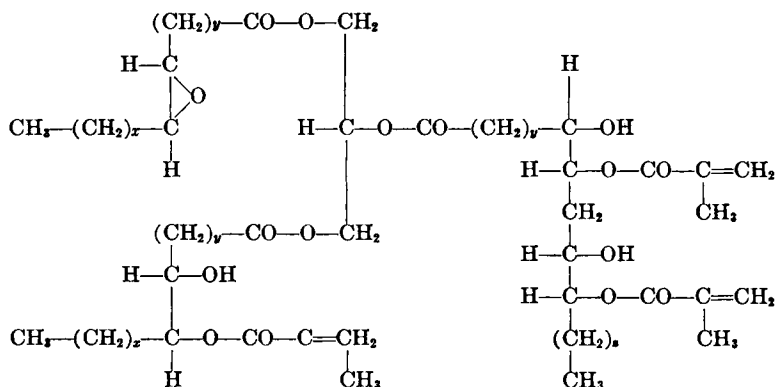
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### INTRODUCTION

Most of the common di- or polycarboxylic acids react in bulk with epoxidized soybean oil (ESBO) to form solid, crosslinked, condensation polymers. Such compositions are disclosed by a Belgian patent issued to Swift and Company.<sup>1</sup> Similar work at this laboratory revealed many practical difficulties in fabricating such mixtures to useful plastics.

New vinyl oil monomers have been prepared by combining epoxidized unsaturated oils with vinyl carboxylic acids. This is accomplished by heating the reactants in the presence of free radical inhibitors and appropriate reaction catalysts. The reaction consists of cleavage of the oxirane ring followed by addition of the vinyl acid through its carboxylic group. By varying the reactants and the conditions of reaction, a large family of related, but different, vinyl oil monomers can be prepared.

Methacrylic acid combines with ESBO to form the following schematized structure:



These vicinal methacryloxy-hydroxy soy oil monomers are not pure compounds. The ESBO raw material is a mixture of triglycerides containing partially and completely epoxidized fatty acid aliphatic chains, a few of which contain acetoxy or formoxy substituents. Using conditions for incomplete reaction, portions of the epoxy groups remain intact in the vinyl

oil monomers. Conversely, using conditions for complete reaction, portions of the epoxy groups can combine with themselves or with hydroxyl groups to form ether linkages in the products. Some of the fatty acid aliphatic chains of the glyceride may contain more than one vicinal methacryloxy-hydroxy substitute while others contain none. The soy oil monomers may be prepared completely free of unreacted methacrylic acid or with varying amounts of this reactant present in the final product. Fortunately, all components are completely compatible, both in the soy oil monomers and in polymers formed from them. An attractive and valuable feature of these soy oil monomers is the presence of reactive functional groups in addition to vinyl unsaturation. The hydroxyl, epoxy, and carboxyl groups in the products may be used for a variety of modifications and for polymer cross-linking reactions.

Vicinal methacryloxy-hydroxy soy oil monomers are clear, yellow, medium viscosity (2,000–2,500 cpoise), high molecular weight (1300–1500) liquids. The monomers readily homopolymerize by a free radical mechanism to clear, solid, thermoset resins. They are compatible and copolymerize with a variety of vinyl monomers, such as acrylic and methacrylic acids and esters, styrene and substituted styrenes, vinyl acetate, vinyl stearate, acrylonitrile, butadiene, allyl compounds, fumarate esters, etc. These copolymers range from highly viscous liquids through soft gels, to tough rubbery products and hard resins.

The copolymers are useful broadly as protective coatings, textile and paper additives and sizing agents, laminating resins, casting and extruding resins, stabilizer-plasticizers, sealing compounds, binders, and adhesives. Applications development work is in progress in several of these areas.

Although initial emphasis has been on the development of oil monomer products based on soybean oil, the synthetic reaction involved is equally applicable to the preparation of reactive vinyl monomers from a large variety of epoxidized animal and vegetable oils and epoxidized fatty acid derivatives, such as alcohols, esters, amides, and nitriles.

## EXPERIMENTAL

### Preparation of Oil Monomers

A series of soy oil monomers was prepared as follows, varying only the ratio of methacrylic acid (MAA) to epoxidized soybean oil (ESBO). Zinc hydrosulfite catalyst (0.004 mole/mole oxirane oxygen) was dispersed in the ESBO. Sufficient *p*-methoxyphenol (MEHQ) was dissolved in the MAA to make a level of 0.06 wt.-% in the total reaction mixture. The ESBO and MAA were mixed and heated at 126–128°C. for 1.5 hr. with continuous stirring and air sparging. Small samples were taken at one-half hour intervals and analyzed for acid and oxirane content. From these analyses the mole per cent values for methacrylation and for oxirane content were calculated, based upon the original moles of oxirane oxygen in the ESBO reactant. Figures 1 and 2 show the progress of the reaction. Under these

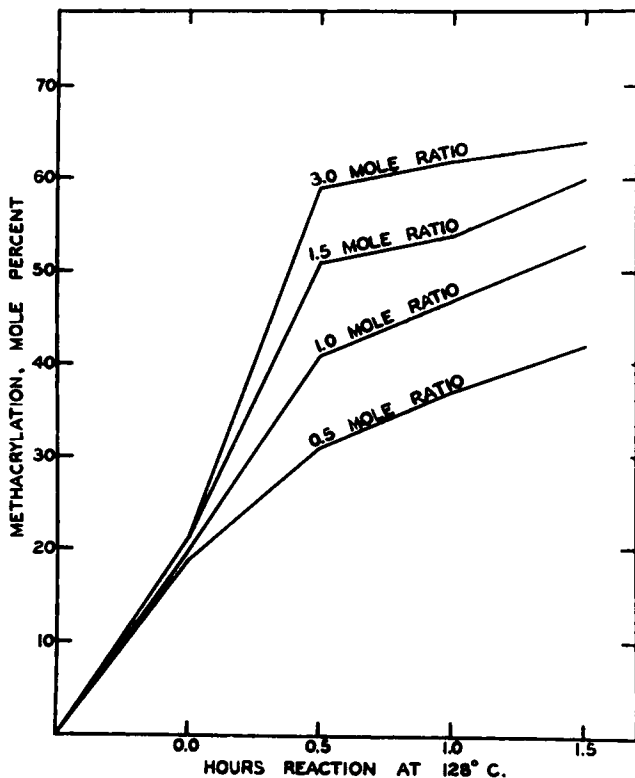


Fig. 1. Reaction of methacrylic acid with epoxidized soy oil at different mole ratios.

conditions, maximum methacrylation was 62–64 mole-%, at which level essentially no oxirane oxygen remained. This level of methacrylation is not unexpected since upon cleavage the oxiranes can react not only with the MAA but also with the hydroxyl groups formed and with themselves to form ether linkages.

At the completion of the 1.5 hr. reaction period at 128°C., 0.02 wt.-% hydroquinone was added to the reaction mixture. The pressure was reduced and unreacted MAA was distilled from the preparation. The plan was to reduce each preparation to a level of about 5 wt.-% MAA. Inadvertently, the 3.0 mole ratio preparation was reduced only to 10 wt.-% MAA.

### Polymer Castings

Clear polymer castings,  $0.125 \times 10 \times 10$  in., were formed from these soy oil monomers, with and without added comonomers. Polymerization was initiated with 1% benzoyl peroxide and the castings were cured at 60°C. for 16 hr.

Table I lists the different polymer castings formed from this series of soy oil monomers and presents some physical data obtained with the castings.

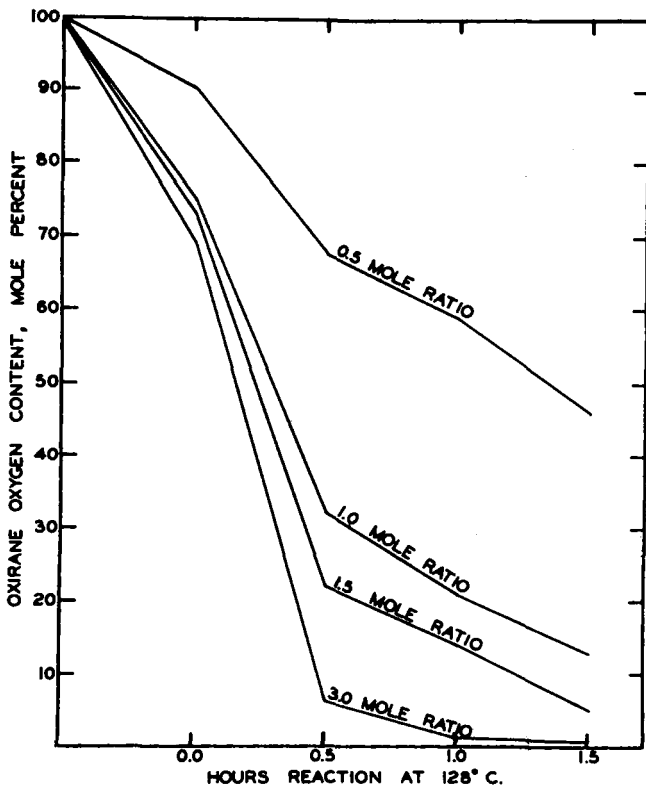


Fig. 2. Reaction of methacrylic acid with epoxidized soy oil at different mole ratios.

The data show not only the variation of physical properties with monomer composition, but also indicate that these vicinal methacryloxy-hydroxy soy oil polymers have properties which could be useful in a variety of applications.

The effect of several different vinyl comonomers on the properties of polymers formed from some of these vicinal methacryloxy-hydroxy soy oil monomers is shown in Table II. Copolymers with styrene and methyl methacrylate are surprisingly similar. Methacrylic acid copolymers have considerably greater hardness and stiffness. Interestingly, they still maintain water resistance and show considerably increased heptane resistance with increasing methacrylic acid content.

Table III shows the effect of outdoor weathering on various copolymer castings of these methacryloxy-hydroxy soy oil monomers. Test panels were exposed at Decatur, Illinois. Note that copolymer castings high in methacrylic acid comonomer alone are prone to craze after extended outdoor weathering. However, copolymer castings, containing 10-20% MAA comonomer plus 33% styrene comonomer, show no change except slight fading after 36 months' outdoor weathering.

TABLE I  
Physical Characteristics of Polymer Castings of Different Preparations of Vicinal Methacryloxy-Hydroxy Soy Oil Monomers

Monomer		Comonomer		Hardness Barcol 935 Initial 10 sec.	Clash-Berg softening temperature, °C. <sup>a</sup>	Solvent resistance			
MAA/ESBO mole ratio	MAA, wt.-%	Oxirane, wt.-%	Material			Wt.-%	Water % Wt. change		Hexane % Wt. change
						7 day	Dried	7 day	Dried
0.5	5.8	2.77	None	0	-3	1.41	-0.12	7.30	-8.86
0.5	10.0	2.64	None	0	25	1.46	0.07	11.20	-5.35
0.5	20.0	2.35	None	42 27	115	1.55	0.07	7.06	0.09
1.0	5.7	0.56	None	16 0	52	1.34	-0.07	11.00	-0.62
1.0	10.0	0.53	None	40 24	79	1.30	-0.02	9.15	1.50
1.0	20.0	0.47	None	64 58	136	1.40	0.11	1.30	0.28
1.5	5.8	0.21	None	28 7	62	1.59	-0.10	10.30	0.33
1.5	10.0	0.20	None	44 30	86	1.33	-0.04	5.90	1.68
1.5	20.0	0.18	None	64 58	139	1.29	0.02	0.76	0.05
3.0	10.0	0.03	None	31 12	65	1.36	-0.04	10.20	1.22
3.0	20.0	0.03	None	63 56	130	1.50	0.05	1.44	0.26
0.5	20.0	2.35	Styrene	61 56	65	0.86	0.00	10.30	2.58
0.5	20.0	2.35	Styrene	70 66	68	0.52	-0.02	10.02	4.90
1.0	20.0	0.47	Styrene	74 69	93	0.72	0.03	0.58	0.10
1.0	20.0	0.47	Styrene	75 72	90	0.49	0.02	1.28	0.42
1.5	20.0	0.18	Styrene	73 69	97	0.75	0.02	0.24	-0.02
1.5	20.0	0.18	Styrene	73 70	94	0.50	0.00	0.20	0.00
3.0	20.0	0.03	Styrene	71 67	89	0.80	0.00	0.32	0.00
3.0	20.0	0.03	Styrene	75 70	86	0.57	0.00	0.21	0.00

<sup>a</sup> Elastic modulus = 10,000 psi.

TABLE II  
Physical Characteristics of Several Different Copolymer Castings of Vicinal Methacryloxy-Hydroxy Soy Oil Monomers

Monomer		Oxirane, wt.-%	Comonomer		Hardness Barcol 935		Clash- Berg softening tempera- ture, °C. <sup>a</sup>	Solvent resistance				
MAA/ ESBO mole ratio	MAA, wt.-%		Material	Wt.-%	Initial	10 sec.		7 Day	Dried	Water % Wt. change	Dried	7 Day
1.0	11.2	0.46	None		47	35	100	0.82	-0.26	3.62	0.60	0.60
1.0	11.6	0.64	Methacrylic acid	33.0	85	84	180 <sup>b</sup>	1.08	-0.04	0.04	-0.51	-0.51
1.0	11.6	0.64	Styrene	33.0	65	56	76	0.56	0.00	0.09	-0.06	-0.06
1.0	11.2	0.46	(Styrene 25.0) (Methacrylic acid 25.0)	25.0)	82	80	142	0.60	-0.24	-0.02	-0.40	-0.40
1.5	18.5	0.05	None		72	65	150	0.74	-0.37	0.25	-0.45	-0.45
1.5	18.5	0.05	Styrene	33.0	74	67	102	0.63	0.02	0.24	-0.05	-0.05
1.5	18.5	0.05	Styrene	50.0	74	68	86	0.46	0.00	0.25	-0.05	-0.05
1.5	18.5	0.05	Methyl methacrylate	33.0	76	70	103	1.04	0.02	0.33	-0.13	-0.13

<sup>a</sup> Elastic modulus = 10,000 psi.

<sup>b</sup> Value at 26,000 psi.

TABLE III  
Outdoor Weathering Exposure Tests on Vicinal Methacryloxy-Hydroxy Soy Oil Polymer Castings<sup>a</sup>

MAA/ESBO mole ratio	Monomer		Comonomer		Gross physical changes	
	MAA, Wt.-%	Oxirane, Wt.-%	Material	Wt.-%	21 Months	36 Months
1.5	5.8	0.21	None		V. sl. yellowing Sl. yellowing	Sl. fading; sl. gloss loss; sl. stiffening No color change; sl. gloss loss; v. sl. crazing
1.5	10.0	0.20	None		Sl. yellowing	Sl. yellowing; sl. gloss loss; sl. crazing
1.5	20.0	0.18	None		No change	V. sl. fading
1.5	20.0	0.18	Styrene	33.0	V. sl. yellowing	V. sl. yellowing; v. sl. gloss loss
1.5	20.0	0.18	Styrene	50.0	Sl. yellowing	Sl. yellowing; v. sl. crazing
1.5	18.5	0.05	Me. methacrylate	33.0	No change	Fading; v. sl. gloss loss
1.0	11.2	0.46	None	33.0	Sl. yellowing	Sl. fading
1.0	11.6	0.64	Styrene	33.0	Sl. yellowing	Sl. fading; sl. gloss loss; considerable crazing
1.0	11.6	0.64	Methacrylic acid	33.0	Sl. yellowing	V. sl. yellowing
1.0	11.2	0.46	(Styrene Methacrylic acid)	(25.0) (25.0)	V. sl. yellowing	

<sup>a</sup> Exposed at Decatur, Illinois; 45° south.

### Determination of Oil Vinylation

Two methacryloxy-hydroxy soy oil monomers were prepared using different reaction conditions. Table IV shows the conditions and the analyses of the products. The method for determining the total vinyl unsaturation present was developed using near infrared spectrophotometry.<sup>2</sup> From these analyses the calculated mole per cent reaction values of Table V were obtained.

TABLE IV  
Chemical Analyses of Typical Methacrylated Soy Oil Monomers

Monomer Prep. <sup>a</sup> no.	MAA/ ESBO mole ratio	Reaction		Acidity, meq./g.	Sapon., meq./g.	Oxirane oxygen, meq./g.	Total vinyl, meq./g. <sup>b</sup>
		Time, min.	Temp., °C.				
45	1.5	30	150	2.41	6.14	0.06	3.76
46	1.5	60	135	2.44	6.12	0.07	3.78

<sup>a</sup> Total reactants 1512 g.; 4 moles of ESBO based on oxirane content.

<sup>b</sup> Near infrared spectrophotometric analysis.

TABLE V  
Reaction Calculations Based on Analyses of Methacrylated Soy Oil Monomers

Monomer prep. no.	Oxirane reacted, mole-%	Acid reacted, mole-% <sup>a</sup>	Methacrylic acid, wt.-%	Total vinyl, % of original <sup>b</sup>	Oil vinylation, mole-% <sup>c</sup>
45	97.7	58.7	20.8	94.7	50.8
46	97.4	58.0	21.1	95.5	50.4

<sup>a</sup> Based on acidity analysis.

<sup>b</sup> Based on total vinyl analysis.

<sup>c</sup> Based on total vinyl minus acidity.

Calculations of the mole per cent vinylation of the oil based on this spectrophotometric analysis average about 8 mole-% lower than calculations of the methacrylic acid reacted based upon acid analysis. Since the analyses for total vinyl are less than that present in the original reactants, these lower mole per cent vinylations may be due to imperfections in our method of analysis.

### Catalysts For Monomer Preparation

Over 50 different compounds were tested as catalysts for the reaction of MAA with ESBO. Although the reaction time was substantially reduced by a number of the catalysts, rapid reaction was not obtained below 110°C. Tertiary butyl titanate, zinc iodide, and tetramethylammonium chloride were three of the most effective catalysts, but each produced dark colored products. The quaternary ammonium salt, like a number of the compounds tested, initiated vinyl polymerization, thereby gelling the monomers.



The reaction time for complete oxirane cleavage at 128°C. was reduced from 3 hr. without a catalyst to 1.5 hr. with zinc dust catalyst. This led to the investigation of metallic sulfite reducing salts such as the zinc hydro-sulfite used in the varying ratio of reactants study. A related salt, basic zinc sulfoxylate formaldehyde,  $Zn(OH)-HSO_2-CH_2O$ , is effective at the low level of 0.0016 mole/mole of oxirane, and produces light yellow products.

### Polymerization Inhibitors For Monomer Preparation

Over 35 compounds were tested for their ability to inhibit vinyl polymerization during the preparation of the soy oil monomers. Ideally, an inhibitor should be thermally and chemically stable in the reaction mixture, yet still give protection against free radicals. Furthermore, it must be effective at such low concentrations that the residual inhibitor in the soy oil monomer product can be overcome readily by common polymerization initiators.

The common phenolic free radical inhibitors, hydroquinone (HQ) and *p*-methoxyphenol (MEHQ), proved to be as satisfactory as any. Table VI shows considerable difference in the effects of these two inhibitors on the rate of polymerization of vicinal methacryloxy-hydroxy soy oil.

TABLE VI  
Effect of Inhibitor on Cure Rate of a Methacryloxy-Hydroxy Soy Oil Copolymer\*

Inhibitor	Wt.-%	Curing time		
		Induction, hr.	Max. exotherm, hr.	Total, hr.
MEHQ	0.050	0.50	1.15	2.95
HQ	0.035	2.50	3.40	5.00

\* Formulation: 75 parts Soy oil monomer (containing 12% MAA), 25 parts styrene, 1 part benzoyl peroxide; cured in a 60°C. oil bath; samples 3 in. depth in a 16 mm. O.D. test tube.

In practice, the specified ideal requirements were not met by the use of organic free radical inhibitors alone. By combining oxygen or air with an organic free radical inhibitor, vinyl polymerization was effectively suppressed, even at the elevated temperatures of the acylation reaction. This resulted in products which were reactive vinyl monomers, yet had good storage stability.

### Monomer Molecular Weight

The molecular weight of several soy oil monomers was determined in order to ascertain the extent of vinyl polymerization during monomer preparation. A cryoscopic method<sup>3</sup> was used. The solvent chosen was benzene saturated with water at 5°C. in order to prevent pick-up of water from the atmosphere. Table VII presents the experimentally determined

molecular weights for three different preparations and compares each with the calculated theoretical molecular weight for the corresponding vicinal methacryloxy-hydroxy soy oil. Each experimental value represents a mean of three replicates. Sample 3 was included since chemical and physical analyses indicated that partial vinyl polymerization had occurred during its preparation. The higher molecular weight bears this out.

TABLE VII  
Molecular Weights of Methacryloxy-Hydroxy Soy Oil Monomers

Sample no.	Methacrylation, mole-%	Methacrylic acid, wt.-%	Theoretical mol. wt.	Experimental mol. wt.
1	36	0.52	1050	1560
2	70	1.55	1040	1240
3	36	0.43	1060	2690

### Acrylated Soy Oil Monomers

Vinyl oil monomers were similarly prepared using acrylic acid in place of methacrylic acid. For comparison two examples are presented in Table VIII. The reactions were faster and higher levels of vinylation were obtained. These monomers were copolymerized with 33 wt.-% styrene in 0.125 in. thick sheet castings. Table IX presents some of the physical properties obtained with these copolymer castings. Notice that the acrylated soy oil polymers are considerably softer and more flexible than the corresponding methacrylated soy oil monomers.

TABLE VIII  
Chemical and Physical Characteristics of Two Vicinal Acryloxy-Hydroxy Soy Oil Monomers

AA/ESBO mole ratio	Acrylic acid, wt.-%	Oxirane oxygen, wt.-%	Acrylation, mole-%	Oxirane reacted, mole-%	Viscosity, poise <sup>a</sup>	Refractive index $n_D^{25}$
1.0	7.9	0.48	65	90	183	1.4698
1.5	14.5	0.59	75	89	74	1.4662

<sup>a</sup> At 23°C.

### CONCLUSIONS

This work resulted in the development of an oil monomer product which forms tough, stable, rigid, thermoset copolymers with other vinyl monomers. The monomer is prepared by combining ESBO (1 mole of oxirane content) with methacrylic acid (1.5 moles containing 0.025% MEHQ), hydroquinone (0.04% of total reactants), and basic zinc sulfoxylate formaldehyde (0.0016 mole). The mixture is reacted at 150°C. for 30 min. with continuous mixing and slow air sparging. The product, cooled to 25°C., is a yellow liquid, viscosity 2000–2500 cpoise,  $d_4^{25}$  1.030,  $n_D^{25}$  1.4645.

TABLE IX  
Physical Characteristics of Polymer Castings of the Vicinal Acryloxy-Hydroxy Soy Oil Monomers

Monomer		Comonomer		Hardness		Clash-Berg softening temperature, °C. <sup>a</sup>	Solvent resistance					
AA/ESBO, mole ratio	AA, wt.-%	Oxirane, wt.-%	Material	Wt.-%	Barcol 935		Initial	10 sec.	Water % wt. change	7 day	Hexane % wt. change	7 day
1.0	7.9	0.48	None			20	0	45	1.59	-0.08	7.84	0.08
1.0	7.9	0.48	Styrene	33.3		60	53	56	0.88	0.05	4.00	1.90
1.5	14.5	0.59	None			50	37	58	2.04	-0.02	2.55	0.58
1.5	14.5	0.59	Styrene	33.3		68	63	71	0.91	0.11	0.81	0.28

<sup>a</sup> Elastic modulus = 10,000 psi.

Typical analyses are as follows: acidity, 2.50 meq./g.; saponification, 6.10 meq./g.; oxirane oxygen, 0.10 meq./g.; total vinyl, 3.75 meq./g.

This soy oil monomer (prepared with inhibitors) is stable when stored at room temperature in the dark. Numerous samples have remained unchanged for several years. However, it polymerizes to a hard, clear, cross-linked solid within several hours when exposed to the sunlight. It may also be homo- or copolymerized with other vinyl monomers at room or elevated temperatures using common free radical initiators.

Typical physical properties of a 33 wt.-% styrene copolymer casting, initiated with benzoyl peroxide and cured at elevated temperature, are shown in Table X.

The copolymer properties indicate certain unique features contributed by the methacryloxy-hydroxy soy oil comonomer. The high flexibility, tough-

TABLE X

Property	ASTM	
Barcol 934-1 hardness		
Initial		25
10 sec.		18
Clash-Berg softening temp., °C. (Elastic modulus = 10,000 psi)	D-1043	95
Heat distortion		
(66 psi), °C.	D-648	86
(264 psi), °C.		76
Impact strength	D-256	
Izod, ft.-lb./in. of notch		0.4
Unnotched charpy, ft.-lb./in. of face		7.5
Taber abrasion loss, mg./1000 cycles (Calibrae CS17 abrasive wheels, 1000 g. wt. on each)		65
Tensile strength, psi	D-638	7,300
Tensile modulus, psi	D-638	370,000
Tensile elongation, %	D-638	12
Flexural strength, psi	D-790	12,300
Flexural modulus, psi	D-790	325,000
Flexural deflection, in.	D-790	>2.0
Water absorption, wt.-% (30 days at 25°C.)	D-570	0.6
Chemical resistance	D-543	
Acids		Good
Weak bases		Good
Strong alkalies		Poor
Most organic solvents (except some chlorinated hydrocarbons and acetone)		Fair
Outdoor weathering (at Decatur, Illinois; 45° south; 36 months' exposure)		
Benzoyl peroxide-initiated		Very slight fading
Methyl ethyl ketone peroxide-cobalt naphthenate-initiated		Slight fading, slight development of a pink coloration

ness, and abrasion resistance coupled with good tensile strength and good flexural strength are unusual in crosslinked copolymers. Water resistance is good, and tests have shown good retention of strength after extended immersion in boiling water. Outdoor weather resistance is excellent, and no stabilizers are required for protection against ultraviolet light. No depolymerization is observed when heating at 500°F. Tests have shown excellent adhesion to glass. During cure, peak exotherms are low, and cure times may be adjusted over wide ranges by using suitable polymerization initiator systems.

## TOXICOLOGY

For over three years personnel have worked regularly with these vinyl soy oil monomers. There have been no observed toxicity symptoms or any allergic skin reactions. Tests with rabbits showed skin irritation under conditions of constant contact which disappeared upon removal of the vinyl soy oil monomer. Inhalation tests with rats did not show any physical irritation. Administration of the methacryloxy-hydroxy soy oil monomer to the eyes of rabbits produced severe irritation and some damage.

We are indebted to Drs. A. W. Turner and D. C. DeLong for the performance and evaluation of the toxicity tests. Our appreciation to Dr. T. F. Protzman, Dr. J. A. Wagoner, and Mr. A. D. Summers for physical testing of the copolymer castings.

## References

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2. Goddu, R. F., *Anal. Chem.*, **29**, 1790 (1957). A modification of this method was developed by Dr. R. M. Powers of this laboratory.
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## Synopsis

New vinyl oil monomers have been prepared by combining epoxidized unsaturated oils with vinyl carboxylic acids. This is accomplished by heating the reactants in the presence of free radical inhibitors and appropriate reaction catalysts. The reaction consists of cleavage of the oxirane ring followed by addition of the vinyl acid through its carboxylic group. By varying the reactants and the conditions of reaction, a large family of related, but different, vinyl oil monomers can be prepared. Vicinal methacryloxy-hydroxy soy oil monomers are clear, yellow, medium viscosity (2000–2500 cpoise), high molecular weight (1300–1500) liquids. Chemical analyses are presented for typical preparations. The monomers readily homopolymerize by a free radical mechanism to clear, solid, thermoset resins. They are compatible with a variety of commercial vinyl monomers and form copolymers which range from highly viscous liquids through soft gels, to tough rubbery products and hard resins. Data are presented on physical properties of copolymer castings of several specific vicinal methacryloxy-hydroxy soy oil monomers.

### Résumé

De nouvelles huiles monomériques vinyliques ont été préparées en combinant des huiles insaturées époxydées avec des acides carboxyliques vinyliques. Ceci est réalisé par chauffage des réactifs en présence d'inhibiteurs de réactions radicalaires et de catalyseurs appropriés. La réaction consiste en une rupture du noyau oxirane suivie de l'addition de l'acide vinylique au niveau de la fonction carboxylique. En variant les réactifs et les conditions opératoires il est possible de préparer une série importante d'huiles monomériques vinyliques de type semblable. Les huiles de soya monomériques à groupes méthacryloxy-hydroxy vicinaux sont des liquides limpides jaunes de viscosité moyenne (2000 à 2500 cp) et de poids moléculaire élevé (1300 à 1500). Des analyses chimiques sont données pour des préparations typiques. Les monomères polymérisent aisément par un mécanisme radicalaire. Les résines obtenues sont des produits clairs et solides et thermodurcissables. Elles sont compatibles avec une variété de monomères vinyliques de haute viscosité aux produits élastiques durs et aux résines dures en passant par des sels peu consistants. Des données concernant les propriétés physiques des objets en copolymères obtenus aux dépens de diverses huiles monomériques spécifiques de soya à groupes méthacryloxy-hydroxy vicinaux sont présentées.

### Zusammenfassung

Neue Vinylölmomere wurden durch Reaktion von epoxydierten ungesättigten Ölen mit Vinylkarboxylsäuren dargestellt. Diese Reaktion wird durch Erhitzen der Ausgangsprodukte in Gegenwart von Inhibitoren für radikalische Polymerisation und von geeigneten Katalysatoren durchgeführt. Die Reaktion besteht in einer Spaltung des Oxiranringes, gefolgt von einer Addition der Vinylsäure über ihre Karboxylgruppe. Durch Variierung der Reaktionsteilnehmer und Reaktionsbedingungen kann eine grosse Gruppe verwandter, aber doch verschiedener Vinylölmomere dargestellt werden. Vicinale Methacryloxy-Hydroxy-Sojaölmomere sind klare, gelbe, hochmolekulare Flüssigkeiten von mittlerer Viskosität (2000–2500 cp). Chemische Analysen für typische Präparate werden mitgeteilt. Die Monomeren polymerisieren leicht radikalisch zu klaren, festen, wärmehärtenden Harzen. Sie sind mit einer Vielfalt von handelsüblichen Vinylmonomeren verträglich und bilden Copolymere, die sich von hochviskosen Flüssigkeiten über weiche Gele bis zu zähen, kautschukartigen Produkten und harten Harzen erstrecken. Daten für die physikalischen Eigenschaften einiger Copolymergieharze aus einigen spezifischen, vicinalen Methacryloxyhydroxy-Sojaölmomeren werden angegeben.

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