

# Reactions of Unsaturated Fatty Alcohols. XIII. Copolymers of Unsaturated Fatty Vinyl Ethers and Cyclic Monomers<sup>1</sup>

E. J. DUFEK, L. E. GAST, and H. M. TEETER, Northern Regional Research Laboratory,<sup>2</sup> Peoria, Illinois

## Abstract

Conjugated linseed, conjugated soybean, and nonconjugated linseed vinyl ethers were copolymerized with various cyclic comonomers. The comonomers used were dihydroabietyl, cyclohexyl, 5-norbornene-2-methyl, di- and tetrahydrodicyclopentadienyl vinyl ethers, and cyclo- and methylcyclopentadiene.

All copolymers containing a cyclic comonomer gave baked films that are distinctly superior to unmodified drying oils or vinyl ether homopolymers in hardness and alkali resistance. Several of these copolymers air-dried overnight to moderately hard, wrinkle-free films.

The improvement in hardness and alkali resistance may be caused by the steric effects of the cyclic comonomers. These hold the fatty side chains apart thus increasing the proportion of intermolecular to intramolecular crosslinking.

POLYMERS and copolymers of vinyl ethers of linseed and soybean alcohols show much promise as protective coatings, especially as baked finishes for metal. Outstanding characteristics include alkali resistance, flexibility, adhesion, and heat resistance. Although these film properties are superior to those of many coatings based on linseed and soybean oils and their derivatives, the behavior of vinyl ether polymers during drying suggested that optimum film properties, anticipated because of the chemical constitution of these materials, were not being achieved.

Molecular weight distribution studies (1) on soybean vinyl ether homopolymers showed that half of the molecular species in a typical homopolymer having a number average molecular weight of 4,800 had molecular weights of 7,000 or above. Such values correspond to about 25 and more vinyl units in the polymer chains. These polymers therefore have extremely high functionality with respect to oxidizable, unsaturated side chains, and they would be expected to dry with extreme rapidity. Nevertheless, homopolymers of linseed and soybean vinyl ethers and their copolymers with saturated alkyl vinyl ethers (such as ethyl, isobutyl, or 2-ethylhexyl vinyl ethers), either did not dry at room temperature or produced soft, tacky films. Relatively high baking temperatures (200C and above) were required to obtain promising films. Furthermore, prolonged bakes at lower temperatures did not produce films equivalent to those resulting from short bakes at high temperatures.

Another problem encountered with vinyl ether polymers was oxidative attack of the chains at points near the ether linkages. Study of this problem (2) revealed that esters and even free fatty acids were formed, thereby accounting for the poor alkali resistance of films in which this oxidative degradation had occurred. Long bakes at low temperatures (100–150C) appeared to aggravate degradation, whereas relatively little degradation was observed in films

produced by short bakes at 200C and above. Once a good film was formed, oxidative degradation did not appear to progress at a significant rate.

One approach to improving properties of vinyl ether films was to use comonomers capable of crosslinking during either polymerization or subsequent film formation. The copolymerization of allyl vinyl ether, 1,2-divinyloxyethane, or 2-vinylxyethylmethacrylate with fatty vinyl ether (3) gave films with better alkali resistance and hardness, but the improvement was not as great as was expected.

The inability of fatty vinyl ether polymers and copolymers to form films having good properties may be caused in part by loss of unsaturation previously observed during polymerization (4,5). Some of this loss represents crosslinking decreasing mobility of the polymer side chains. Structures of this type formed during polymerization would reduce the ability of the remaining polyunsaturation in the fatty side chains to undergo intermolecular crosslinking necessary for satisfactory film formation. Intramolecular reaction may also occur during polymerization and film formation. For example, in a soybean vinyl ether homopolymer, a chain of 25 units consists of a backbone of 50 carbon atoms with 25 side chains attached to alternate atoms; each side chain has a chain length of 18 carbon atoms plus 1 oxygen atom. Coiling of these side chains probably leads to a tangled network such that much of the unsaturation would not be in positions favorable for crosslinking with side chains of other similar polymer molecules; thus, at low baking temperatures, mobility of the polymer side chains would be less, and intramolecular combination could occur at the expense of intermolecular crosslinking necessary to give an optimum film. However, high baking temperatures would favor increased mobility of polymer side chains, thus facilitating the intermolecular crosslinking reaction. Once an adequate amount of cross linking was established, susceptible ether linkages would be contained deep within the molecule and would be further protected from oxidative degradation.

The basic problem, then, in obtaining vinyl ether films with optimal properties was to find ways of reducing steric interference of unsaturated side chains and increasing their mobility so that adequate intermolecular crosslinking can take place readily. One method would be to prepare copolymers with appropriate bulky comonomers in the expectation that these bulky groups, interspersed among the fatty side chains, would tend to hold the fatty chains apart, block intramolecular reaction both during polymerization and subsequent film formation, and facilitate their movement into positions favorable for intermolecular crosslinking. The purpose of this paper is to report on the preparation of copolymers of fatty vinyl ether and several cyclic comonomers and on the effects of these comonomers on the drying and film properties of the copolymers.

## Discussion

Conjugated linseed vinyl ether, soybean vinyl ether, and nonconjugated linseed vinyl ether were copoly-

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<sup>2</sup> A laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S.D.A.

TABLE I  
 Physical and Film Properties of Copolymers of Fatty Vinyl Ethers and Cyclic Monomers

Monomers			Physical properties		Film properties <sup>a</sup>			
Cyclic M <sub>1</sub>	Fatty vinyl ether M <sub>2</sub>	Mole % of M <sub>1</sub>	Molecular wt	Viscosity <sup>b</sup> (100% solids)	Mn drier (0.05%)		No drier	
					Hardness Sward	Resists 5% NaOH	Hardness Sward	Resists 5% NaOH
.....	Conj. soybean	0	5700	89	8	1	6	5
.....	Conj. linseed	0	3920	98	6	24	6	24
"Abitol" vinyl ether	Conj. linseed	25	.....	420	8	168	4	312
		50	1890	..... <sup>c</sup>	18	312	12	312
		75	1410	..... <sup>c</sup>	50	312	60	312
"Cyclol" vinyl ether	Conj. soybean	25	.....	160	14	240	6	48
		50	.....	720	12	312	8	312
		75	3340	..... <sup>c</sup>	12	366	14	336
"Cyclol" vinyl ether	Conj. linseed	25	.....	222	10	168	4	168
		50	3500	990	10	192	8	288
		75	4000	..... <sup>c</sup>	16	288	38	288
Cyclohexyl vinyl ether	Conj. linseed	25	.....	98	8	216	4	216
		75	.....	..... <sup>c</sup>	16	216	10	216
Dihydrodicyclopentadienyl vinyl ether	Conj. soybean	50	5000	1680	14	72	10	24
		75	3180	..... <sup>c</sup>	28	144	36	144
Dihydrodicyclopentadienyl vinyl ether	Conj. linseed	25	3260	440	10	48	2	240
		50	5000	5100	16	144	10	144
		75	2700	..... <sup>c</sup>	26	240	32	240
Dihydrodicyclopentadienyl vinyl ether	Nonconj. linseed	25	.....	48	34	24	10	24
		75	5900	..... <sup>c</sup>	66	96	72	96
Tetrahydrodicyclopentadienyl vinyl ether	Conj. linseed	25	3550	249	8	120	4	140
		75	2750	..... <sup>c</sup>	24	240	32	240
Methyl dihydrodicyclopentadienyl vinyl ether	Conj. soybean	50	945	44	8	168	2	120
		75	1020	2850	52	168	44	168
Methyl dihydrodicyclopentadienyl vinyl ether	Conj. linseed	75	.....	2300	48	120	30	168
Cyclopentadiene	Conj. soybean	75 <sup>d</sup>	2220	2220	14	288	6	288
Cyclopentadiene	Conj. linseed	75 <sup>d</sup>	2740	2040	16	288	16	288
Cyclopentadiene	Nonconj. linseed	75 <sup>d</sup>	3130	35	36	48	28	144
Methylcyclopentadiene	Conj. soybean	75	1740	..... <sup>c</sup>	22	144	14	144
Methylcyclopentadiene	Conj. linseed	75	.....	..... <sup>c</sup>	20	168	26	72

<sup>a</sup> Baked 10 min at 200C.<sup>b</sup> Time in sec for the bubble (100% solids) to rise 7.5 cm in a Gardner-Holdt viscosity tube at 25C. (Z<sub>0</sub> is 195 sec).<sup>c</sup> Too viscous to flow.<sup>d</sup> Charge comprised 75 mole % cyclopentadiene and 25 mole % fatty vinyl ether. Based on I.V., composition was 60 mole % cyclopentadiene.

merized with varying proportions of dihydrodicyclopentadienyl, tetrahydrodicyclopentadienyl, dihydroabietyl ("Abitol"), 5-norbornene-2-methyl ("Cyclol"), and cyclohexyl vinyl ether and cyclo- and methylcyclopentadiene. Representative data on the properties of films prepared from the copolymers are given in Table I, which includes data on soybean and linseed vinyl ether homopolymers for comparison. It is evident that an outstanding improvement in hardness (Sward) and alkali resistance was achieved by the use of cyclic comonomers. This improvement may result from any one or any combination of the following factors.

First, the improvement in film hardness appears to be directly related to the weight percent of the cyclic monomer incorporated into the copolymer. For example, with conjugated linseed copolymer films containing drier, a small group, like either "cyclol" or cyclohexyl, increased the film hardness from approximately 8 to 16 as the wt % of the cyclic material was increased from 14 to 61 (25 to 75 mole %). With larger bicyclic groups, e.g., di- and tetrahydrodicyclopentadienyl groups, hardness increased from 8 to 26 (16 to 64 wt %) while dihydroabietyl vinyl ether, the largest incorporated into the copolymers, increased film hardness from 8 to 50 as its wt % was increased from 29 to 79 (25 to 75 mole %).

Unsaturation in the cyclic comonomer may not be necessary since the vinyl ethers of di- and tetrahydrodicyclopentadienyl alcohol (75 mole % level) are equally effective in improving film properties when copolymerized with linseed vinyl ether.

Films of copolymers of conjugated linseed vinyl ether with dihydrodicyclopentadienyl vinyl ether or cyclopentadiene have alkali resistance superior to that of films obtained from the corresponding non-

conjugated linseed vinyl ether copolymers. Perhaps additional condensation reactions (possibly of the Diels-Alder type) may have occurred between the conjugated system of the fatty vinyl ether and the unsaturation in either the cyclic structure or another conjugated linseed group. Since the cyclohexyl and tetrahydrodicyclopentadienyl groups are saturated, the condensation reactions must occur between two conjugated linseed groups.

 TABLE II  
 Film Hardness of Air-Dried, Conjugated, Fatty Vinyl Ether Copolymers

Monomers		Mole % M <sub>1</sub>	Hardness <sup>a</sup> (Sward units)
Cyclic M <sub>1</sub>	Fatty vinyl ether, M <sub>2</sub>		
Cyclopentadiene.....	Linseed	60	28
Cyclopentadiene.....	Soybean	60	34
Dihydrodicyclopentadienyl vinyl ether.....	Linseed	75	28
Tetrahydrodicyclopentadienyl vinyl ether.....	Linseed	75	16
"Cyclol" vinyl ether.....	Linseed	50	12
"Abitol" vinyl ether.....	Linseed	50	4

<sup>a</sup> After 18 hr at room temperature with 0.01% cobalt and 0.5% lead driers as naphthenates.

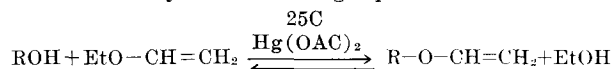
The actual amount of fatty side chains available for intermolecular crosslinking is lower in the copolymers than in the fatty vinyl ether homopolymers, thus, the total amount of crosslinking may be little different in the two polymer types. Since the homopolymers of cyclic monomers are white amorphous solids that give hard (but brittle), alkali-resistant films, it appears that the bulky cyclic groups effectively hold the reactive fatty groups apart and permit a higher ratio of intermolecular to intramolecular crosslinking to take place, thereby improving film properties. Any reduction in intramolecular reaction reduces the plasticizing agents in the film, and

as a result the increased hardness gives a more desirable film.

Copolymers of cyclic comonomers with conjugated fatty vinyl ethers gave films that would air-dry at room temperature (Table II). This property also supports the idea that unsaturation in the fatty group is easily available for crosslinking reaction. The properties of air-dried films were sufficiently promising to justify some additional evaluation studies as architectural enamels and wood finishes. Preliminary data show that many of these copolymers respond to baking schedules at relatively low temperatures. Studies on the evaluation of these copolymers for several specific end uses are in progress and are the subject of a recent publication (6).

### Experimental

**Starting Materials.** Dihydrodicyclopentadienyl alcohol was prepared by hydration of dicyclopentadiene (7); bp 96–99C/0.5 mm;  $n_D^{20}$  1.5228; I.V.: Calcd. 169.4; found, 172.5. Tetrahydrodicyclopentadienyl alcohol was prepared by hydrogenation of dihydrodicyclopentadienyl alcohol at 1,000 lb pressure using 10% palladium on charcoal; bp 69–72C/0.15 mm;  $n_D^{20}$  1.5090; I.V. 0.8; Anal.: Calcd. for  $C_{10}H_{16}O$ : C, 79.1; H, 10.5; found: C, 78.76; H, 10.65; "Abitol" (Hercules Powder Company), "Cyclol" (Interchemical Corporation), and cyclohexyl alcohol were used as received. The alcohols were converted to the corresponding vinyl ethers by modification (8) of Watanabe's procedure (9,10) for *trans*-etherification. This reaction is illustrated by the following equation:



Increased yields were obtained by the following step: After the reaction mixture reached equilibrium, the mixture was washed free of ethanol, dried with sodium sulfate, and transvinylated again by addition of fresh catalyst. Distillation from potassium carbonate and redistillation from KOH (dissolved in methanol) gave the vinyl ethers shown in Table III.

Conjugated soybean (99.6%) and conjugated linseed vinyl ether (99.5%) were prepared from the fatty alcohols Unadols 40 and 90 (Archer-Daniels-Midland Co.) as previously described (11).

Nonconjugated linseed vinyl ether (100%) was also prepared as previously described (12).

Cyclopentadiene (bp 41–42C) and methylcyclopentadiene (bp 71–73C) were prepared from corresponding dimers (Enjay Corporation) by the dropwise addition of the dimer into mineral oil at 270–280C. The monomer was collected in a receiver cooled with a mixture of solid  $CO_2$  and acetone.

**Preparation of Polymers and Copolymers.** Cationic polymerization at room temperature was carried out as described (13), and modified by Mustakas *et al.*

TABLE III  
Properties of Cyclic Vinyl Ethers

Vinyl ether	bp	$n_D^{20}$	Purity*
"Abitol".....	152–155C/ 0.15 mm	1.5124	87.5
"Cyclol".....	65–67C/ 8.0 mm	1.4767	96.6
Cyclohexyl.....	78–79C/ 7.0 mm	1.4489	95.7
Dihydrodicyclopentadienyl.....	68–70C/ 0.4 mm	1.5035	98.6
Tetrahydrodicyclopentadienyl.....	57–59C/ 0.2 mm	1.4928	97.9
Methyl dihydrodicyclopentadienyl.....	85–87C/ 0.15 mm	1.5020	91.7

\* See Reference 11.

TABLE IV  
Effect of Catalyst Concentration on Copolymerization of Cyclopentadiene with Conjugated Linseed Vinyl Ether<sup>a</sup>

SnCl <sub>4</sub> Mmole <sup>d</sup>	Iodine value <sup>b</sup>	Composition of product, mole % cyclo- pentadiene	Viscosity <sup>c</sup> (100% solids)
1.8	149.4	47.5	83 sec
3.6	154.2	50.0	1500 sec
5.4	163.0	54.5	Rubbery
6.0	182.1	60.0	Rubbery

<sup>a</sup> Charge comprised 75 mole % cyclopentadiene and 25 mole % conjugated linseed vinyl ether.

<sup>b</sup> I.V. of conjugated linseed vinyl ether homopolymer was 104.2. Catalyst used was 1.8 mmole/100 g monomer.

<sup>c</sup> Time in sec for bubble to flow 7.5 cm in a Gardner-Holdt viscosity tube.

<sup>d</sup> Mmoles SnCl<sub>4</sub>/100 g of comonomers in 300 ml of toluene.

(14). Polymerization was carried out according to the general procedure: The comonomers (50 g) dissolved in toluene (3 ml/g of comonomers) were placed in a flask fitted with a stirrer, recording thermocouple, and nitrogen inlet tube. A solution of 8% stannic chloride in toluene (3 ml/50 g of comonomers) was added to initiate the polymerization reaction. The temperature rose steadily and at the maximum temperature (5 to 120 sec) the reaction was quenched by adding methanol (10 ml), calcium hydroxide (4 g), and water (1.5 ml). After filtration the products were isolated by removal of the solvent under reduced pressure.

Vinyl ethers of the various alcohols were completely copolymerized and appeared in the copolymer in the same ratio as in the initial charge. Cyclopentadiene however was only partially copolymerized along with all the fatty vinyl ether. Based on iodine value, the copolymer contained approximately 50 mole % cyclopentadiene, whereas 75 mole % cyclopentadiene was present in the initial charge. The amount of catalyst used under these polymerization conditions effected both the composition and the molecular weight of the copolymer (Table IV). The use of 1.8 mmoles of stannic chloride per 100 g of comonomers resulted in copolymerization of only 30% by weight of the cyclopentadiene in the initial charge, and gave a copolymer of lower molecular weight as judged by viscosity measurements. Increasing the amount of catalyst used increased both viscosity and the proportion of cyclopentadiene incorporated into the copolymer. For film studies a copolymer containing 60 mole % (25 wt %) of cyclopentadiene was used.

The composition of the methylcyclopentadiene copolymers could not be determined from its I.V. These copolymers gave I.V.'s much higher than those calculated. For example, a linseed vinyl ether copolymer containing 75 mole % methylcyclopentadiene had an I.V. of 286, as compared to the calculated I.V. of 214.

Attempts to copolymerize dicyclopentadiene and conjugated linseed vinyl ether by using toluene or dicyclopentadiene as the solvent gave only a homopolymer of conjugated linseed vinyl ether.

All copolymers were water-white to pale yellow in color. Those containing 50 mole % or less of cyclic monomer were viscous oils, whereas those containing 75 mole % cyclic comonomer were tacky, rubbery solids. All copolymers were soluble in hydrocarbon and chlorinated hydrocarbon solvents.

**Preparation of Films and Film Properties.** Solutions of the copolymers were prepared by dissolving 1 g of the copolymer in 3 g of toluene, Manganese drier (0.05% as naphthenate) was added, and films, 1 mil thick when dry, were cast on steel plates. The films were baked with and without drier in an electric oven at 200C for 10 min and then allowed to cure 18 hr at room temperature before determining hard-

ness and alkali resistance. Air-dried films were cast with lead-cobalt drier (0.5% lead and 0.01% cobalt as naphthenate) and allowed to dry 18 hr at room temperature. Table I shows the results of Sward hardness and resistance to 5% NaOH (3) on some of the baked copolymer films; Table II shows the Sward hardness of the air-dried copolymer films. The color of the test spot of the cyclic vinyl ether copolymer changed only slightly during the test period. Films of cyclopentadiene fatty vinyl ether copolymers in contact with alkali changed rapidly and became dark brown in a few hours.

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## Reactions of Unsaturated Fatty Alcohols. XIV. Preparation and Properties of Styrenated Fatty Vinyl Ether Polymers<sup>1</sup>

WILMA J. SCHNEIDER, L. E. GAST, A. W. SCHWAB, and H. M. TEETER, Northern Regional Research Laboratory,<sup>2</sup> Peoria, Illinois

#### Abstract

New polymeric products have been prepared from conjugated linseed vinyl ether polymers and styrene. Up to 64% by weight of styrene can be incorporated by heating the preformed fatty vinyl ether polymer and monomeric styrene in an aromatic solvent. Primary factors influencing the course of the reaction were molecular weight and peroxide content of the starting vinyl ether polymer, reaction temperature, and type of solvent used. Formation of heterogeneous reaction products and gelation were encountered unless styrene was consumed in the reaction or removed.

Films of these styrenated vinyl ether polymers show improved properties over the homopolymers previously studied. Baked films exhibit better gloss, color, and hardness; are more thoroughly cured; and show good flexibility and adhesion. Their resistance to 5% aqueous alkali is outstanding. The films also exhibit air-drying properties.

Fatty vinyl ether polymers and copolymers have shown only limited compatibility with commercial resins. However, styrenated polymers are compatible with long oil alkyd, urea, epoxy, hydrogenated rosin, and polyurethane resins.

chemical resistance, and flexibility could be controlled.

Styrenated oils and alkyd resins made from a variety of drying oils have been known for many years (7). Some of the advantages claimed are faster drying, improved durability, excellent water and alkali resistance, light color, and good electrical resistance (8).

Preparation of copolymers of fatty vinyl ethers with styrene, therefore, seemed a logical approach because such copolymers might show improvement over the fatty vinyl ether polymers and copolymers prepared previously. However, direct copolymerization of fatty vinyl ethers with styrene using cationic catalysts was not successful. The products were almost exclusively polyvinyl ethers as shown by infrared analyses. Consequently, grafting styrene into the preformed fatty vinyl ether polymers or copolymers in a manner similar to that used in styrenating oils or alkyd resins, was investigated as an alternative method. This paper reports styrenation of polymers derived from conjugated linseed fatty vinyl ethers. Films from these new products have good hardness, flexibility, gloss, adhesion, and excellent alkali resistance.

#### Experimental

**Starting Materials.** A low molecular weight polymer of conjugated linseed vinyl ether was prepared in USP chloroform containing 0.5 to 1.0% ethanol and using stannic chloride as catalyst (2). Analytical data on the polymer were as follows: Molecular weight (4), approximately 1,500; viscosity, 4.8 poises (25°C); conjugated diene, 31.8%; iodine value, 114. Medium molecular weight conjugated linseed polymer was prepared in toluene using stannic chloride catalyst (2). Analyses: Molecular weight (4), approximately 4,000; viscosity, 125 poises (25°C); conjugated diene, 34.8%; iodine value, 109.

Commercial styrene polymer grade was distilled to

**A**N EXTENSIVE STUDY has been in progress at the Northern Laboratory on unsaturated fatty vinyl ether polymers and copolymers derived from soybean and linseed alcohols (1-3,5,9,10). Films made from these derivatives have shown promise as protective coatings, especially for metals. Copolymers have been prepared in which both the type and amount of comonomers with the fatty vinyl ethers have been varied to produce films whose properties such as hardness,

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<sup>2</sup> A laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S.D.A.