

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.

remove any inhibitor. Toluene and xylene were C.P. grade and were used without further purification.

**Preparation of Styrenated Products.** Fatty oils and alkyds are usually styrenated by either the mass or solventless method, or the solvent method. Styrenations were effected in aromatic hydrocarbon solvents, as the mass method resulted in gelled products before sufficient styrene was incorporated. In general, the reaction of fatty vinyl ether polymers and styrene was carried out as follows: One part of polymer was mixed with three parts of styrene in three parts of toluene or xylene (all parts by weight) while stirring and heating at 95C (unless otherwise specified) until the viscosity of the reaction solution rose sharply. At this point, the reaction was stopped since continued heating caused the mixture to gel. Hydroquinone (0.1 to 0.3% by weight) was added to preserve the product. Viscosities were measured by observing the length of time in seconds required for the reaction solution to pass through 160 mm of a 1 mm capillary tubing.

Styrene content was determined as follows: A 0.5 g sample of the reaction mixture was weighed into an aluminum dish and baked in a carbon dioxide atmosphere for 10 min at 200C to drive off all volatile materials. The inert atmosphere was necessary since unstyrenated polymers baked in air at these temperatures lost considerable weight, whereas similar samples baked under carbon dioxide lost less than 2% of initial weight. The per cent by weight of styrene in the final product was calculated by subtracting the weight of the polymer (P), known to be present initially from the weight of total nonvolatile solids (SP) in the styrenated product, and dividing by (SP). Hence: % Styrene =  $\frac{SP - P}{SP} \times 100$ .

**Preparation of Films.** Solutions of styrenated products were adjusted to 25% solids and drawn down on steel panels 4 x 8 x .032 in (Q panels) with a doctor blade so that a dry film thickness of 1 mil was obtained. The panels were dried at room temperature or baked in air in an electric oven at various temperatures. The drier system, when used, was 0.01% Co + 0.5% Pb as naphthenates. Films were evaluated for Sward rocker hardness, pencil hardness, and resistance at 5% aqueous alkali.

### Results and Discussion

The reaction of fatty oils, bodied oils, and alkyd resins with styrene has been the subject of many investigations (6-8). While opinion differs as to the reactions involved, several factors have been elucidated and serve as a guide for our work. We found that the polymerization of styrene with fatty side chains was influenced by the molecular weight of the fatty material, amount of catalyst present (peroxides), reaction temperature, type of unsaturation (conjugated vs. nonconjugated), and type of solvent.

**Molecular Weight.** The molecular weight of the starting oil derivative apparently is one of the more critical factors. Hewitt and Armitage (6) have shown that bodied oils increase in viscosity much earlier in

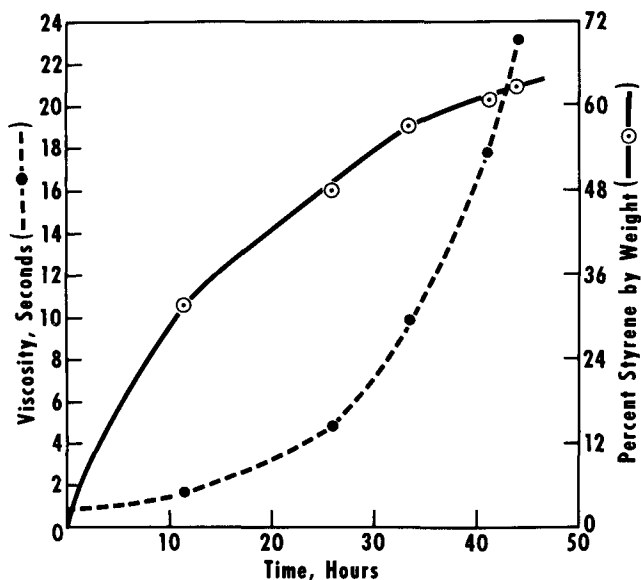


Fig. 1. Plot of viscosity vs. reaction time and styrene incorporation vs. time of a low molecular weight linseed polymer.

the styrenation reaction than nonbodied or low viscosity oils, thus resulting in more rapid gelation of the product. Our observations (Table I) on conjugated linseed vinyl ether polymers showed they behave similarly. If no crosslinking took place, we might expect a plot of viscosity vs. time to remain essentially constant or increase slightly with time. This expectation did not occur (Fig. 1). Evidently crosslinking becomes appreciable during the later phases of the reaction and leads to gelation of the product. A plot of the styrenation of a medium molecular weight polymer would be similar, except that much less crosslinking would be required to produce a significant increase in viscosity. Gelation would then occur at a shorter reaction time and effectively cut off further reaction with styrene.

**Peroxide Content.** Another factor affecting the preparation of styrenated products is the amount of peroxide in the polymer. To study the effect of this variable on the styrenation of a linseed vinyl ether polymer, we developed peroxides in the polymer by bubbling oxygen through the sample in toluene at 25C until the desired level of oxidation was achieved. Results of styrenating a series of oxidized medium molecular weight polymers (4,000) in toluene at 95C in an inert atmosphere are shown in Table II. Reactions were carried to a viscosity of 40 sec. These data show that polymers with a high peroxide value shorten the reaction time required to reach the specified viscosity although the amount of

TABLE II  
Effect of P.V. on the Styrenation of Linseed Polymers

Peroxide value <sup>a</sup>		Reaction time at 95C, hr <sup>b</sup>	Weight per cent styrene <sup>c</sup>
Medium mol. wt.	Low mol. wt.		
80	....	1.25	12
50	....	3.5	19
33	....	4.5	24
18	....	26	28
11	....	37	33
6	....	52	38
....	140	13	52
....	67	44	49
....	23	62	55
....	4	76	64

<sup>a</sup> Wheeler method.

<sup>b</sup> Time required to reach a viscosity of 40 sec with medium molecular weight polymers and 20 sec for low molecular weight polymers.

<sup>c</sup> Styrene available for incorporation was 75%.

TABLE I

Effect of Polymer Mol. Wt. on Per Cent Styrene Incorporated

Molecular weight	Viscosity (Gardner-Holt)	Reaction time at 95C, hr <sup>a</sup>	Weight per cent styrene <sup>b</sup>
>5,000	Z <sub>6</sub>	8.5	10.7
4,000	Z <sub>3</sub>	11	27.6
1,500	R-S	44	49.0

<sup>a</sup> To incipient gelation.

<sup>b</sup> Styrene available for incorporation was 75%.

TABLE III

Effect of Temperature on Styrenation of Conjugated Linseed Vinyl Ether Polymers

Exp. No.	Molecular weight	Peroxide value <sup>a</sup>	Reaction temp, C	Reaction time, hr <sup>b</sup>	Weight per cent styrene <sup>c</sup>
A.....	Low	60	138	1	54
B.....	Low	60	100	44	49
C.....	Medium	3	120	2	29
D.....	Medium	3	95	36	34
E.....	Medium	60	100	3.5	19

<sup>a</sup> Wheeler method.<sup>b</sup> Time required until rapid viscosity increase occurred.<sup>c</sup> Styrene available for incorporation was 75%.

TABLE IV

Change in Composition of Styrenated Linseed Polymer on Aging at 25C

Sample age, months	Weight Per Cent Styrene <sup>a</sup>		
	Sample 1	Sample 2	Sample 3
0	37.5	34.1	64.2
3	45.3	45.1	64.5
5	60.8	57.5	67.2
10	.....	.....	68.9
16	.....	.....	71.2

<sup>a</sup> Styrene available for incorporation was 75%.

TABLE V

Baked Film Properties of a Styrenated Linseed Polymer

Styrene content, %	Baking cycle, °C/min	Hardness (Rocker)	Resists 5% NaOH, hr
0	205/30	44	6
0	205/30 <sup>a</sup>	28	48
30	205/30	18	8
30	205/30 <sup>a</sup>	18	>144
30	232/15	28	48
30	232/15 <sup>a</sup>	18	>224

<sup>a</sup> Contained 0.01% Co + 0.5% Pb drier.

TABLE VI

Properties of Air-Dried Films<sup>a</sup>

Styrene content, %	Hardness		Alkali resistance, <sup>c</sup> days
	Rocker	Pencil <sup>b</sup>	
19 <sup>d</sup>	12	>6 (5)	F4
38 <sup>d</sup>	8	3-5 (1)	>9
49 <sup>e</sup>	12	6 (8)	F20
55 <sup>e</sup>	12	6 (8)	>15
64 <sup>e</sup>	22	6 (7)	F20

<sup>a</sup> Contained 0.01% Co + 0.5% Pb drier.<sup>b</sup> Numbers in parentheses indicate number of days curing before pencil tests were conducted.<sup>c</sup> F - Failed; 5% aqueous NaOH.<sup>d</sup> Sample of medium molecular weight polymer used for styrenation.<sup>e</sup> Sample of low molecular weight polymer used for styrenation.

TABLE VII

Compatibility of Styrenated Linseed Vinyl Ether Polymer

Resin	1:1 Solution compatibility <sup>a</sup>	Baked film compatibility <sup>b</sup>
Nitrocellulose.....	I	.....
Long oil linseed alkyd.....	C	Smooth tough film
Acrylic.....	I	.....
Pliolite VT.....	I	.....
Phenolic.....	I	.....
Urea.....	C	Smooth tough film
Styrene-butadiene.....	C	.....
Epoxy.....	I	Smooth tough film
Polyamide.....	H	Apparent incompatibility
Parlon.....	I	.....
Polyvinyl acetate.....	I	.....
Styrenated alkyd.....	I	.....
Hydrogenated Rosin.....	C	Smooth tough film
Polyester.....	I	.....
Medium oil soya alkyd.....	H	Hazy film
Short oil soya alkyd.....	H	Hazy film
Vinyl acetate-chloride.....	I	.....
Polyurethane.....	C	Smooth tough film
Melamine.....	I	.....
Silicone.....	C	Incompatible

<sup>a</sup> I = Incompatible. C = Compatible. H = Hazy.<sup>b</sup> Films baked at 232C for 15 min.

The effect of the peroxide value on the styrenation of a low molecular weight (1,500) conjugated linseed vinyl ether polymer was also studied (Table II). These reactions were carried to a viscosity level of 20 sec. A high peroxide value polymer incorporates about 50% by weight of styrene in a shorter time than a polymer with a low peroxide value, indicating that with low molecular weight polymers the rate of the styrenation reaction was significantly increased by higher concentrations of peroxides. With medium molecular weight polymers, the increased rate of reaction obtained with high peroxide value materials cannot be used to advantage because the viscosity increases rapidly before much styrene has reacted.

**Temperature.** In the styrenation of vinyl ether polymers of both low and medium molecular weights and higher temperatures (120-138C) significantly shorten the time required to reach a sharp increase in viscosity (Table III). With the low molecular weight polymers some advantage is gained by operating at these higher temperatures since more styrene is reacted in a shorter time than at 100C. Also, since gelation is less of a problem, polymers with higher peroxide values may be used to increase further the rate of reaction. Higher temperatures also shorten the reaction time with medium molecular weight polymers. However, 120C may be slightly high to obtain maximum utilization of the styrene because the experiment conducted at 95C gave a more highly styrenated product (see experiments C and D, Table III). A comparison of the styrenation of medium and low molecular weight products reveals that with the latter more styrene can be incorporated at either temperature (compare A with C and B with D). The trend shown by A and B suggests that more styrene may perhaps be incorporated into the low molecular weight polymer by operating at even higher temperatures.

**Product Stability.** Gelation usually occurred after the styrenated products had stood at room temperature from several weeks to several months. The usefulness of these products would be greatly enhanced if their shelf life could be prolonged. Analyses of the reaction solutions revealed that the excess monomeric styrene was slowly reacting with the product causing gelation. Table IV shows the increase in styrene content with time of three selected samples. The first two samples containing excess monomeric styrene had partially gelled after 3 months of aging at room temperature. After 5 months these samples were completely gelled, whereas the last sample has remained stable for 16 months. Incorporation of all or nearly all the styrene during the initial reaction thus appears to give stable products. Stability of products containing excess monomeric styrene could not be improved even when hydroquinone was added to inhibit further reaction.

**Film Properties.** Significant improvement in film properties was achieved by the styrenation of conjugated linseed vinyl ether polymers. Table V shows that a polymer containing 30% styrene has greatly improved alkali resistance, especially when driers are incorporated. The increased hardness and alkali resistance when the higher baking temperature (232C) was used, are possibly caused by better through-dry and curing of the film.

Styrenated polymers will air-dry at room temperature in several days to give hard, alkali-resistant films. The properties of these air-dried films are shown in Table VI. Films 24 hr old were soft (pen-

styrene incorporated under these conditions was low. Certainly high peroxide values favor crosslinking reactions as evidenced by the short period of time required for a rapid increase in viscosity.

oil hardness = 1 or 2), but hardness increased on further curing of the films to the values shown. Hardness and resistance to alkali were improved by increasing styrene content of the polymer.

Preliminary results of evaluation tests (11) indicate that films of a styrenated conjugated linseed polymer, when baked at either 205°C for 30 min or 232°C for 15 min, had excellent flexibility and resistance to reverse impact. Styrenated linseed polymers showed good compatibility with TiO<sub>2</sub>.

**Compatibility.** Perhaps the most significant new property of the styrenated polymers is their compatibility with a number of commercial resins. Nonstyrenated vinyl ether polymers and copolymers were almost entirely incompatible with 20 selected commercial resins at polymer-to-resin ratios of 1:9, 1:1, and 9:1 (11). Such incompatibility greatly limits the use of vinyl ethers because they cannot be blended with other coating materials to modify their properties. A styrenated conjugated linseed vinyl ether polymer containing 30% styrene by weight is compatible at the 1:1 ratio with a number of commercial resins (Table VII). One unusual feature of this styrenated linseed polymer is that it is incompatible with other vinyl ether polymers and other styrene-containing resins, such as styrene-butadiene or styrenated alkyd resins.

Since these new products exhibit outstanding alkali resistance and compatibility with commercial resins, better methods of preparation leading to improved stability of the products should be sought.

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## Isothiocyanates from Enzymatic Hydrolysis of *Lesquerella* Seed Meals<sup>1</sup>

M. E. DAXENBICHLER, C. H. VanETTEN, H. ZOBEL, and I. A. WOLFF,  
Northern Regional Research Laboratory,<sup>2</sup> Peoria, Illinois

#### Abstract

Enzymatic hydrolyzates from seed meals of 17 species of the genus *Lesquerella*, family Cruciferae, were examined for thiooxazolidones and volatile isothiocyanates. Quantitative estimates of the total volatile isothiocyanates, calculated as butenyl, ranged from 0.6 to 13.0 mg per g of solvent-extracted meal. No thiooxazolidone was found. By means of paper chromatography, melting point, and X-ray patterns of the thiourea derivatives, the volatile isothiocyanates, 3-methylthiopropyl-, 4-methylthiobutyl-, and 6-methylthiohexyl-, were shown to be present in the hydrolyzates from three species. Evidence for identity of isothiocyanates in hydrolyzates from the remaining species was obtained by paper chromatography of the thiourea derivatives.

widespread occurrence of isothiocyanate-yielding glucosides in the crucifer family is well known (11). Beta-hydroxyisothiocyanates after enzymatic liberation from the glucose spontaneously cyclize to thiooxazolidones, which adversely affect thyroid activity in animals. Volatile isothiocyanates (mustard oils) impart unpalatability to meals if present in sufficient amount and furthermore may be toxic. To our knowledge no literature information concerning the presence of these compounds in *Lesquerella* is available other than the investigation of a single species at this laboratory (1). For these reasons a study of derived isothiocyanates in seeds from *Lesquerella* species was undertaken.

#### Methods

Seed meals were prepared by grinding the seed in a 6-in hammer mill with 1/16-in, round-hole screen followed by extraction in a Butt apparatus with petroleum ether (pentane-hexane bp 33-57°C).

Hydrolysis of the meals and estimation of the liberated thiooxazolidones and volatile isothiocyanates were performed according to the methods described by Wetter (9,10) except that the volatile isothiocyanates were collected in a larger volume of ammonia without the presence of silver nitrate. An aliquot of this distillate was treated with silver nitrate to determine total volatile isothiocyanate. The remainder was used for paper chromatography of the thioureas

SEED OF THE GENUS *Lesquerella*, family Cruciferae, yields oil containing hydroxy fatty acids of potential industrial importance (7). Utilization of the protein-containing meal as feed is obviously desirable if commercialization of a species of *Lesquerella* as an oilseed occurs. The amino acid composition of the meal indicates good nutritional quality (8). However,

<sup>1</sup> Presented in part to the American Chemical Society, Chicago, Ill., September 3-8, 1961.

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