on these ester fractions than was possible on the total lard esters. The greatest numerical variations in percentages are those for methyl stearate and methyl oleate. This may be due mainly to normal experimental errors in measuring the peak areas, since one or the other of these esters is present in three fractions in amounts requiring attenuation of the detector signal. It should be noted that although one lard was commercially rendered, another rendered in the laboratory, and the third solvent extracted each contained the same components. It is concluded, therefore, that the components are naturally occurring and not produced as artifacts in the rendering process.

A comparison of the polyunsaturated acids found in the three lards as determined by GLC on the fractions and by the ultraviolet spectrophotometric method on the total esters is shown in Table II. Good agreement was obtained even for the tetraenes and pentaenes. The small differences in composition between the three lards by the fractionation procedure are not considered significant and probably are the result of normal errors involved in measuring peak areas and in adding the internal standard. The use of auxiliary fractionation by silicic acid and the use of GLC on the fractions obtained affords a means of quantitative estimation of minor components as well as major components of complex fats.

TABLE II

Polyunsaturated Acid Composition of Three Lards by GLC and U.V. Spectrophotometry

	Commercial lard		Lab. rendered lard		Solv. extracted lard	
	U.V.[a]	GLC[b]	U.V.[a]	GLC[b]	U.V.[a]	GLC[b]
	%	%	%	%	%	%
Diene	12.2	11.1	11.6	11.2	11.6	10.4
Triene	0.87	0.45	0.78	0.51	0.89	0.51
Tetraene	0.35	0.25	0.26	0.24	0.27	0.26
Pentaene	0.15	0.13	0.11	0.09	0.12	0.12

[a] Determined on total lard methyl esters.

[b] Calculated from chromatograms of fractions obtained by silicic acid column separation of lard methyl esters and use of internal standard.

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Reactions of Unsaturated Fatty Alcohols. XV. Styrenation of Fatty Vinyl Ether Polymers in Terpene Solvents[1]

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Abstract

Styrenation of fatty vinyl ether polymers in dipentene at 145–165C gives products containing from 20 to 67% styrene by weight but little or no unreacted monomeric styrene remained. After 27 months no gelation occurred in these products. Apparently dipentene serves as an effective chain transfer agent during styrenation, keeps the growing polymer chains short, and reduces crosslinking reactions. The amount and type of unsaturation needed in the fatty side chains of the polymer to produce homogeneous products were studied. Ultraviolet and infrared analyses were useful in determining the function of unsaturation in these reactions.

Tests on baked films from these products showed that as the amount of styrene was increased, both hardness and alkali resistance were significantly increased. Films prepared from products containing 34 and 67% styrene had Sward hardness values of 10 and 60, and alkali resistance of 33 days and over 65 days, respectively. Films from products prepared in aromatic solvents *versus* dipentene at the same styrene level showed no difference in hardness, but the alkali resistance of the "dipentene film" was greater.

Introduction

STYRENATION of fatty vinyl ether polymers in aromatic solvents has been reported in a previous publication (6). This work demonstrated that polymers containing grafted styrene produced films with properties much improved in drying, hardness, color, and alkali resistance over films from unstyrenated polymers. Whereas fatty vinyl ether homopolymers produced satisfactory coatings only after baking, the styrenated materials gave films that would air-dry at room temperature. More important, the styrenated products were compatible with such commercial resins as long oil alkyd, urea, epoxy, and polyurethane resins (8). Consequently, blends of styrenated vinyl ether polymers with these resins would give formulators an opportunity to "tailor make" coating materials for a specific end use.

Styrenation of fatty vinyl ether polymers in aromatic solvents presented difficulties that were overcome. Products prepared from low and medium molecular weight polymers gelled either during the reaction or by continued polymerization of the unreacted styrene on aging. Removal of excess monomeric styrene by precipitating the styrenated polymer with methanol and redissolving the product in toluene or xylene produced products that were stable on aging. A simpler method for incorporating monomeric styrene into the polymer during the initial reaction was sought.

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Armitage et al. discussed the use of terpene solvents in the styrenation of several fatty oils (1). These solvents aid in maintaining a lower viscosity level during the reaction thereby allowing essentially all the styrene present to be incorporated into a product without gelation. We developed a procedure which gave stable products that contained from 20 to 67% styrene by weight and that were essentially free of monomeric styrene. These materials were isolated for analyses as 100% solids without gelation.

Experimental

Starting Materials. Cyclic linseed vinyl ether was prepared as follows: Linseed alcohol was heated at 225C for 25 min with 5% potassium hydroxide. The product was distilled and the distillate treated with urea in methanol and the nonadduct cyclic fraction separated from the crystalline adduct. The cyclic alcohol was vinylated at 180–195C for 1 hr using 4% potassium hydroxide catalyst. Distillation of the vinylated mixture gave cyclic linseed vinyl ether; b.p. 149–54C/0.5 mm; n_D^{30}, 1.4838; vinyl ether, 97%; conjugation: diene, 85.5%. This product is a mixture of diene materials where one or both of the double bonds are in or near the ring (3). Conjugated linseed, soybean, and safflower vinyl ether polymers of low molecular weight (*ca.* 1,500) were prepared from the appropriate vinyl ethers in U.S.P. chloroform (solvent) with stannic chloride (catalyst) (2). Product analyses: Linseed—Iodine Value (I.V.), 114; conjugation: diene, 33.6%; triene, 3.9%; soybean—I.V., 89; conjugation: diene, 33.6%; triene, 0.24%; safflower—I.V., 112; conjugation: diene, 62.5%; triene, 0.6%. Copolymers of soybean-cyclic linseed and soybean-safflower vinyl ethers were similarly prepared. Stearyl, oleyl, and nonconjugated linseed vinyl ether polymers were prepared in toluene with stannic chloride catalyst (2). Molecular weights of these polymers were 4,000–5,000, and analyses were: Stearyl—I.V., 0; m.p., 48–9C; oleyl—I.V., 85; nonconjugated linseed—I.V., 185; conjugation: diene, 3.8%; triene, 0.43%.

Commercial polymer-grade styrene was used after distillation to remove the inhibitor. Xylene and toluene were CP grade. Dipentene (Hercules Powder Company) was used without further purification.

Preparation of Styrenated Products. A typical styrenation reaction was carried out as follows. The polymer (1 part), styrene (0.25 to 2.1 parts) and dipentene (2 parts) were placed in a three-necked flask fitted with a stirrer, viscometer, condenser, and thermometer. The reaction was conducted at reflux temperature (145–165C), which depended on the unreacted styrene remaining in the mixture, until either the viscosity (6) showed a sharp increase or all the styrene initially present had reacted. Incorporation of styrene was determined periodically as the reaction progressed (6).

Infrared and Ultraviolet Analyses. The styrenated polymers were difficult to isolate solvent-free because of their high viscosity and their tendency to gel during removal of the last traces of solvent. Samples for analyses were obtained by placing a few drops of the reaction mixture in a small aluminum weighing dish so as to form a thin film on the bottom. The dish was heated in an oven at 200C for 15 min under an atmosphere of carbon dioxide. The residue in the dish was then dissolved in either isooctane or cyclohexane for ultraviolet studies or in carbon disulfide for infrared analysis.

Film Casting and Testing. Polymer films were cast on steel "Q" panels from reaction solutions that had been previously adjusted to contain 1 g of styrenated product to 3 g of solvent. "Drawdowns" were made with a doctor blade set to give a baked film thickness of approximately 1 mil. The baking cycle was 200C for 15 min. A mixed drier (0.01% Co + 0.5% Pb as naphthenates based on polymer weight), when used, was added to the polymer solution before casting the film. Hardness tests were made by the Sward rocker technique and by the pencil test (4). Alkali resistance was measured by placing several drops of 5% aqueous sodium hydroxide on the film and then observing the time required for film failure. Evaporation was prevented by placing a small watch glass over the droplet and sealing the edges with wax.

Discussion of Results

Fatty vinyl ether polymers styrenated under conditions that left excess unreacted styrene in the final reaction mixture gelled in several weeks to several months. Additional work showed that the tendency of the product to gel could be significantly reduced and more styrene could be incorporated when low molecular weight polymers with low peroxide values were used (6). Polymers of this type were selected for study in experiments with dipentene as a solvent.

A series of reactions was studied in which the amount of styrene added to the reaction mixture was varied to determine whether all the monomer initially present could be incorporated into the product. Representative data are shown in Table I. The reaction was carried out for 20 hr in all experiments except D where the reaction was stopped at the end of 14 hr because of a rapid increase in viscosity. Styrenated products containing from 20 to 67% by weight of styrene were readily prepared with little or no monomeric styrene left in the reaction mixture. These products appear to be stable since no gelation has occurred after 27 months' storage at room temperature. All product solutions, as well as films prepared from them, were clear.

TABLE I

Styrenation of Low Molecular Weight Conjugated Linseed Vinyl Ether Polymer (Peroxide Value 9.5) in Dipentene at 165C

Exp.	Reactants (parts by wt)			Product		
				Wt % of styrene		Viscosity[c] (Gardner)
	Polymer	Dipentene	Styrene	Calc.[a]	Found[b]	
A	10	20	2.5	20	20	<A
B	10	20	5	33	34	<A
C	10	20	10	50	49	C
D	10	20	21	68	67	Z 2

[a] $\frac{\text{Wt styrene initially}}{\text{Wt polymer + wt styrene initially}} \times 100.$

[b] Determined by observing the increase in weight of the nonvolatiles during the reaction (6).

[c] Determined on product solution.

The possibility that these products were simple mixtures of fatty polymer and polystyrene was considered. Compatibility tests were carried out using polystyrene formed during the attempted styrenation of oleyl and stearyl vinyl ether polymers (Table IV). A few drops of this polystyrene in dipentene was added to 2 ml of each of the styrenated product solutions from the conjugated polymers shown in Table I. After mixing, a second phase appeared as small droplets indicating that polystyrene formed under our reaction conditions is not appreciably soluble in the product solution.

Stable, low-viscosity products were also prepared from a solvent mixture containing dipentene and xylene. Table II shows the effect of solvent composition on styrenation when a reaction mixture consisting of 25% polymer, 25% styrene, and 50% solvent is used. In pure xylene the viscosity of the reaction mixture increased rapidly after 4 hr heating and about half of the styrene initially present reacted with the polymer. Addition of 10% dipentene to the solvent mixture increased the reaction time to 8 hr and 80% of the styrene was incorporated into the product. Both of these products gelled after aging several weeks. Increasing dipentene from 25 to 100% of the solvent increased the reaction time from 8 to 17.5 hr while incorporating essentially all the monomeric styrene into the final product. These results illustrate the advantage of using dipentene-rich solvent mixtures to prevent gelation during the reaction.

TABLE II

Styrenation of Low Molecular Weight Conjugated Linseed Vinyl Ether Polymer in Xylene-Depentene Solvents

Solvent composition, wt %		Reaction time,[a] hr	Styrene reacted,[b] wt %	Viscosity, Gardner (product solution)
Dipentene	Xylene			
0	100	4	24	Gelled
10	90	8	40	Gelled
25	75	8	44	X
50	50	14	44	I
100	0	17.5 [c]	49	C

[a] Elapsed time until a rapid viscosity increase was observed.

[b] Maximum possible styrene in product, based on monomer charge, was 50% by wt.

[c] Reaction stopped because essentially all the styrene was consumed. A rapid viscosity increase was not observed.

Dipentene also serves to produce styrenated products of improved stability. Terpene solvents are known to serve as efficient chain transfer agents. Armitage et al. (1) have shown that terpenes compare with carbon tetrachloride in reducing the molecular weight of polystyrene prepared in these solvents. For example, polystyrene prepared in either dipentene or carbon tetrachloride had a molecular weigh of approximately 10,000. Styrene polymerized in xylene, a less efficient chain transfer solvent, gave a polymer with a molecular weight of 100,000. Mayo (5) established a quantitative relationship between the ability of solvents to transfer hydrogen (or chlorine) to the growing styrene radicals by calculating the transfer constant with the polymerization of styrene at 100C. Carbon tetrachloride and dipentene have transfer constants $>7 \times 10^{-3}$; xylene, approximately 5×10^{-4}; and toluene, 7×10^{-5}.

Polymerization of styrene in either xylene or dipentene when conjugated linseed vinyl ether polymer was present, gave a product containing styrene presumably grafted to the polymer. Theoretically the union of styrene (S) with the vinyl ether polymer (VEP) may occur by at least two processes. One process involves chain transfer whereby the growing polystyrene chain ($S_n\cdot$) is terminated by hydrogen transfer with polymer that forms a vinyl ether polymer radical (VEP·) and initiates a new chain.

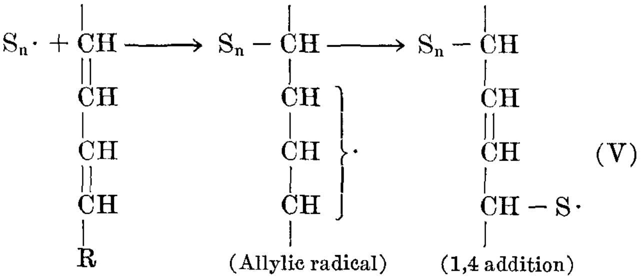
$$\text{VEP} \xrightarrow[\text{or heat}]{\text{Peroxides}} \text{VEP}\cdot \qquad \text{(I)}$$

$$\text{VEP}\cdot + \text{S} \longrightarrow \text{VEP-S}\cdot \qquad \text{(II)}$$

$$\text{VEP-S}\cdot + \text{nS} \longrightarrow \text{VEP-S}\cdot_{n+1} \qquad \text{(III)}$$

$$\text{VEP-S}\cdot_{n+1} + \text{VEP} \longrightarrow \text{VEP-S}_{n+1}\text{H} + \text{VEP}\cdot \qquad \text{(IV)}$$

Reactions II, III, and IV yield a product with one polymer molecule attached to each styrene chain. If this process predominated, no crosslinking would occur and the products would show no tendency to gel. With the second process, polymerization of the growing polystyrene chain may occur through the conjugated diene in the fatty side chains of the polymer, e.g.:



Although only 1,4 addition to the allylic radical is shown, 1,2 addition may also occur.

In xylene (low-transfer constant) an appreciable number of styrene chains may grow long enough by reaction V to contain at least two VEP molecules thus producing crosslinking, an increase in viscosity, and eventual gelation. In dipentene (high-transfer constant) the styrene chains would be kept relatively short by frequent hydrogen transfer with the solvent. Thus, the incorporation of two or more VEP molecules in the polystyrene chain would be less frequent, and only limited crosslinking would occur.

Reaction V would consume conjugated diene present in the polymer. If this process were operating during styrenation, one might expect some loss in diene content. Table III lists preliminary data comparing the diene content of the original polymer with two styrenated products after correcting for the amount of styrene incorporated. During the styrenation of both products, as the amount of styrene increases, the more conjugated diene is lost. With the product containing 34% styrene by weight, 16% of the diene originally present was lost, whereas the product containing 49% styrene lost 20%. Since the addition of styrene to a conjugated system (Diels-Alder reaction) is also possible, the diene loss shown in Table III may not be due entirely to reaction V.

TABLE III

Reduction in Conjugation of Linseed Vinyl Ether Polymers During Styrenation at 165C in Dipentene [a]

Polymer	Conjugation, %			
	Diene		Triene	
	Theory	Found	Theory	Found
Starting	......	32.9	......	3.6
Styrenated:				
34% styrene	21.5	18.0	2.4	1.5
49% styrene	16.9	13.5	1.9	1.1

[a] Reaction mixture composed of one part polymer, one part styrene, and two parts dipentene.

The amount and type of unsaturation in the fatty polymer side chains are of primary importance in the copolymerization reactions with styrene. Not all the fatty vinyl ether polymers copolymerized (Table IV), and polystyrene formed as a second phase in the stearyl and oleyl experiments. Obviously, these materials cannot undergo reaction V since they contain no conjugated diene, and apparently they cannot successfully compete with the solvent in serving as chain transfer agents (reactions II, III, and IV).

TABLE IV

Effect of Unsaturation on the Styrenation of Fatty Vinyl Ether Polymers in Dipentene at 165C[a]

Vinyl ether polymer	Reaction time, hr	Styrene reacted[b] wt %	Remarks
Stearyl	3	30	Reaction product separated into two layers[c]
Oleyl	28	48	Reaction product separated into two layers[c]
Nonconjugated linseed	18	49	Homogeneous reaction product; very cloudy films
Conjugated soybean	5	45	Homogeneous reaction product; slightly cloudy to cloudy films
Conjugated linseed	18	49	Homogeneous reaction product; clear films
Conjugated safflower	27	47	Homogeneous reaction product; clear films

[a] Reaction mixture composed of one part polymer, one part styrene, and two parts dipentene.

[b] Reaction stopped because essentially all the styrene was consumed except stearyl reaction. A rapid viscosity increase was not observed.

[c] Infrared spectrum of the product from the lower layer was identical with spectrum of polystyrene; spectrum of the upper layer after evaporation of solvent was identical with that of the starting vinyl ether polymer.

Styrenation of nonconjugated linseed vinyl ether polymer in dipentene gave a homogeneous reaction solution, but films deposited after solvent removal were very cloudy, indicating the presence of considerable polystyrene. One might expect the nonconjugated polymer to act as a more efficient chain transfer agent than either the stearyl or oleyl polymers since it contains a 1,4 pentadiene system. Thus, it may be able to compete with dipentene in terminating polystyrene chains and may be incorporated, to some extent, into the product *via* reactions II, III, and IV.

Differences were observed in the styrenation of conjugated linseed and soybean polymers. Although both contained approximately 34% conjugated diene, films from the linseed were clear but those from the soybean were cloudy. The apparent difference in reactivity of the linseed polymer with styrene may result from cyclic hexadiene derivatives which are formed from the linolenyl alcohol in linseed alcohols during the preparation of the vinyl ether monomers by a reaction similar to that in which cyclic acids are formed from linseed fatty acids (3,7). However, a safflower polymer containing larger amounts of noncyclic conjugated diene than the soybean product (62.5 *vs.* 34%), gave clear films. To determine the amount of conjugated cyclic diene necessary to yield clear films, a series of cyclic linseed-soybean copolymers were prepared (Table V). The data show that clear films were obtained from the copolymer containing 21.4% conjugated cyclic diene in a total diene of 46.8%. A copolymer containing 46.9% noncyclic conjugated diene was prepared from a suitable mixture of safflower and soybean vinyl ethers. The product obtained from the styrenation of this copolymer gave cloudy films demonstrating the beneficial effect of the cyclic diene in polymers on forming compatable styrenated polymers and films.

TABLE V

Effect of Conjugated Cyclic Hexadiene on the Styrenation of Fatty Vinyl Ether Polymers in Dipentene at 165C

Percent cyclic content in soy copolymer	Percent conjugated diene in copolymer	Percent in styrene product	Comments
0	33.9	45.7	Very cloudy film
10.7	39.7	50.2	Slightly hazy film
21.4	46.8	49.0	Clear film
28.5	51.1	48.5	Clear film
42.7	59.6	47.3	Clear film
0[a]	46.9	46.0	Very cloudy film

[a] Copolymer of safflower and soybean vinyl ether.

Baked film properties from the styrenated products prepared in dipentene (Table VI) show that increasing the styrene content of the polymer improves both hardness and alkali resistance. An unusual property observed was that films baked without drier were significantly harder than those containing drier based on the rocker test. This effect was most pronounced with the films from the product containing least styrene. Pencil hardness tests did not reveal this difference in hardness between films with and without drier. Films prepared from the product containing 67% styrene had the best alkali resistance of any material prepared to date. The increased alkali resistance with increasing styrene content is particularly noticeable with films baked without drier. Table VII shows film properties of styrenated products prepared in a mixed aromatic-dipentene solvent system. Increasing the proportion of dipentene from 25 to 100% has little or no effect on film hardness but significantly improves alkali resistance. Baked film properties of the polymers prepared in dipentene indicated that hardness is somewhat less but alkali resistance is improved over the films from products prepared in aromatic solvents. Films cured in air at room temperature from the products prepared in dipentene have not been studied because of the low volatility of dipentene (bp approximately 175C).

TABLE VI

Hardness and Alkali Resistance of Selected Styrenated Fatty Vinyl Ether Polymers

Percentage styrene	Drier[b]	Film properties[a]		
		Hardness		Resists 5% NaOH days
		Rocker	Pencil	
34	+	10	5	33
	−	46	>6	5
49	+	24	5	43
	−	60	5	13
67	+	60	>6	>65
	−	70	>6	>60

[a] Baked at 200C for 15 min.

[b] 0.01% cobalt + 0.5% lead drier as naphthenates.

TABLE VII

Film Properties of Styrenated Linseed Vinyl Ether Polymers Prepared in a Mixed Solvent System

Solvent, %		Percentage styrene	Film properties[a]	
Dipentene	Xylene		Hardness, rocker	Resists 5% NaOH, days
0	100	49	42	17
25	75	44	22	24
50	50	44	24	28
100	0	49	24	43

[a] Films baked at 200C for 15 min containing 0.01% Co + 0.5% Pb drier.

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