Some Observations on the Polymerization of Styrene in the Presence of Oils

L. B. FALKENBURG, W. H. HILL, and HANS WOLFF, A. E. Staley Manufacturing Company, Decatur, Illinois

STYRENATED oils have assumed a prominent role in the surface coating field. Differences among oils, such as the degree of conjugation and of polymerization and the extent of oxidation, have been recognized as influencing the final properties of the product. In this paper are presented our findings on these relationships.

Experimental

Materials. The oils employed in this study were of commercial grade except as noted below. The conjugated oils were prepared either by the anthraquinone treatment (4) or by the Carbon-Nickel process (12). Isomerized tung oil was obtained by exposing tung oil containing a few crystals of iodine to sunlight for several days. The polymerized oils were prepared in the laboratory from the commercial oils by heat-bodying at 300°C. under carbon dioxide. Blown oils were obtained by passing air at a rate of approximately one liter per minute through the oil at a temperature of 70-80°C.

The styrene was a commercial grade of 99% purity, and it was distilled in an all-glass apparatus just prior to use. Benzoyl peroxide was Eastman Kodak's White Label. Cumene hydroperoxide was of 72.8% purity and was obtained from the Hercules Powder Company. The t-butyl hydroperoxide was of 66.8% purity and was obtained from the Union Bay State Company.

Reaction Technique. The solvent method of copolymerization (7) was used throughout this work. Equal weights of styrene and oil were dissolved in an amount of xylene equal to the combined weight of styrene and oil. The mixtures were refluxed for 16 hours. In some experiments peroxides were added as catalysts.

Analytical Procedures

Iodine Value: The Wijs half-hour method was used.

Viscosity: A Gardner bubble viscometer was used to measure viscosity.

Peroxide Value: The Wheeler method was employed for determining the amount of peroxide in the oils (16).

Conjugation: The degree of conjugation was measured with a Beckmann Quartz Spectrophotometer, Model DU.

Percentage of Solids: The percentage of solids in the reaction mixture was determined by the standard method for determining non-volatile matter in varnishes (5).

Extent of Reaction: The consumption or disappearance of styrene in the reaction was calculated by means of the following equation: $\%$ styrene reacted $= 100\,(S\text{-}50)/50$, where $S =$ the percentage of solids in the reaction mixture.

Results

The results obtained by polymerizing styrene in the presence of various oils are presented in Table I. Alkali-refined soybean and linseed oils did not yield homogeneous products. Similar results were obtained with soybean oils heat-bodied to several viscosities. These results checked with those reported by other investigators (7, 10, 15). However we were surprised to find that conjugated linseed and soybean oils also yielded heterogeneous products for Hewitt and Armitage (7) reported that isomerized linseed oil (Conlinol) reacted smoothly with styrene.

It is evident from Table I that dehydrated castor oil, an oil containing conjugation, did not yield clear, fast drying products unless it was partially polymerized. Consequently we heat-bodied conjugated soybean oil to several viscosities, expecting that the polymerized oils would yield clear, fast drying materials when allowed to react with styrene. This result was not obtained. Interestingly enough, the isomerized soybean oil bodied to a high viscosity produced a more heterogeneous product than the isomerized oil polymerized to an intermediate viscosity.

The results we obtained with tung oil were different in part from those obtained by Armitage, *et al.* (1). In accordance with Armitage we found that only a small amount of styrene polymerized, but our product did not dry to a frosty film. In the case of isomerized tung oil the product was not clear and the films were frosty.

The importance of the viscosity of the oil is evident from the results obtained with blown soybean oils. Low viscosity oils of high peroxide value yielded heterogeneous mixtures while oils of intermediate viscosity yielded products which were clear, but whose films were cloudy or opalescent. However the blown

TABLE I

Effect of Oils on Styrene Polymerization (No Catalyst)

Oil	Type	Properties	Product Characteristics
Soybean	Alkali-refined	Viscosity = A; Iodine value = 133.7	Heterogeneous
Soybean	Heat-bodied	Viscosity = Y	Heterogeneous
Soybean	Heat-bodied	Viscosity = Z-4	Heterogeneous
Soybean	Isomerized (Carbon-nickel)	Viscosity = D; Conjugation = 31.7%	Heterogeneous
Soybean	Isomerized (Anthraquinone)	Viscosity = M; Conjugation = 19.8%	Heterogeneous
Soybean	Isomerized (Anthraquinone)	Viscosity = W; Conjugation = 13.2%	Very cloudy film
Soybean	Isomerized (Anthraquinone)	Viscosity = Z-2; Conjugation = 8.9%	Opaque film
Soybean	Blown	Viscosity = J; Peroxide value = 176	Heterogeneous
Soybean	Blown	Viscosity = T; Peroxide value = 198	Heterogeneous
Soybean	Blown	Viscosity = X; Peroxide value = 161	Cloudy film
Soybean	Blown	Viscosity = Z-1; Peroxide value = 151	Clear—fast drying product
Soybean	Blown	Viscosity = Z-5; Peroxide value = 123	Clear—fast drying product
Soybean	Isomerized-blown	Viscosity = X	Clear—fast drying product
Linseed	Alkali-refined	Viscosity = A; Iodine value = 181.2	Heterogeneous
Linseed	Isomerized (Anthraquinone)	Viscosity = K; Conjugation = 18.5%	Heterogeneous
Dehydrated Castor	....	Viscosity = G-H; Conjugation = 25.6%	Opalescent product
Dehydrated Castor	....	Viscosity = V; Conjugation = 19.7%	Clear—fast drying product
Tung Oil	Raw	Viscosity = J-K	Clear—slow drying product
Tung Oil	Isomerized	Buttery	Cloudy product—frosty film

TABLE II

Effect of Peroxides on the Styrene-Oil Copolymerization

Oil	Type	Amount of Catalyst[a]	Remarks
Soybean	Alkali-refined	None	Heterogeneous product
Soybean	Alkali-refined	10% B.P.	Heterogeneous product
Soybean	Isomerized (Anthraquinone); 19.8% conjugation	None	Heterogeneous product
Soybean	Isomerized (Anthraquinone); 19.8% conjugation	10%	Very cloudy film
Soybean	Blown-Viscosity = I; Peroxide value = 179	None	Heterogeneous product; 89.6% Styrene reacted
Soybean	Blown-Viscosity = I; Peroxide value = 179	5% B.P.	Clear film; 98.1% Styrene reacted
Soybean	Blown-Viscosity = I; Peroxide value = 179	5% C.H.P.	Clear film; 97.1% Styrene reacted
Soybean	Blown-Viscosity = I; Peroxide value = 179	5% t-B.H.P.	Clear film; 98.6% Styrene reacted
Soybean	Blown-Viscosity = Z-4; Peroxide value = 135	None	Clear film; viscosity (50% solids in xylene) = C; 90.5% Styrene reacted
Soybean	Blown-Viscosity = Z-4; Peroxide value = 135	5% B.P.	Clear film; viscosity (50% solids in xylene) = B; 96.8% Styrene reacted
Soybean	Blown-Viscosity = Z-4; steamed under reduced pressure to destroy peroxides Peroxide value = 2.3; Conjugation = 3%	None	Clear-fast drying film; but softer than two preceding films
Linseed	Alkali-refined	None	Heterogeneous product
Linseed	Alkali-refined	5% B.P.	Very cloudy film
Linseed	Alkali-refined	10% B.P.	Clear-tacky film
Linseed	Isomerized (Anthraquinone); 18.5% conjugation	None	Heterogeneous product
Linseed	Isomerized (Anthraquinone); 18.5% conjugation	5% B.P.	Slightly cloudy film
Linseed	Isomerized (Anthraquinone); 18.5% conjugation	10% B.P.	Clear-tacky film
Tung	Raw—Viscosity = J-K	None	Clear-slow drying film; 19.6% Styrene reacted
Tung	Raw—Viscosity = J-K	10% B.P.	Clear-tacky film; 43.6% Styrene reacted

[a] % based on weight of styrene. B.P. = benzoyl peroxide; C.H.P. = cumene hydroperoxide; t-B.H.P. = t-butyl hydroperoxide.

oils of high viscosity produced homogeneous, fast-drying products.

The use of a catalyst changes the nature of the products, as can be readily seen from the results given in Table II. Although untreated soybean oil gave a heterogeneous mixture when 10% benzoyl peroxide was used, linseed oil, in the presence of 5% catalyst, yielded a clear reaction product but one which dried to a cloudy film. With 10% benzoyl peroxide, linseed oil or isomerized linseed oil formed products which dried to clear, tacky films. Isomerized soybean oil under these conditions did not give a clear film. In the case of tung oil the addition of the catalyst resulted in a two-fold increase of styrene polymerization.

Studying the effect of peroxides on blown soybean oils has shown that an oil of low viscosity, yielding a heterogeneous mixture, produced a clear resinous product if the reaction was carried out in the presence of 5% added peroxides. Furthermore the addition of this catalyst also increased the extent of styrene polymerization. With a high viscosity oil the addition of catalyst led to higher styrene consumption, but the product possessed a lower viscosity than the one obtained in the absence of a catalyst. A blown oil of high viscosity which had been practically freed of peroxides by steaming at 200°C. under reduced pressure gave, in spite of the destruction of the peroxides, a clear, fast drying material. The film from this product was softer than the one obtained from the product made from the original blown oil.

Discussion

Hewitt and co-workers (1, 7) proposed that styrene copolymerized with the unsaturated fatty acid radicals of an oil by one of two free radical mechanisms. If the unsaturation were conjugated, the growing styrene chains would be propagated across the conjugated linkages in a manner similar to the copolymerization of styrene and butadiene. On the other hand, if the unsaturation were of the methylene interrupted type, the fatty acid radicals would act as chain initiators or terminators with the active methylene groups as the reactive centers. According to these investigators, an oil should contain a certain proportion of conjugation in order to copolymerize with styrene to a homogeneous product. Harrison and Wheeler (6) however in a study of the polymerization of vinyl esters of fatty acids found that there was little difference, if any, between conjugated and non-conjugated esters.

Our results do not confirm the importance of conjugation for we were not successful in producing homogeneous products with isomerized soybean oils. Our failure to obtain homogeneous reaction products when soybean oils and styrene were allowed to react may be accounted for by assuming that specific positional and geometric isomers of conjugated fatty acids are required. Craig (3) has pointed out that geometric configuration may determine whether or not a conjugated diene will react by polymerization or addition. Some evidence in this reaction concerning the importance of the geometric configuration of the conjugation appears in the examples of tung oil and isomerized tung oil. The differences between the two products of the copolymerization with styrene may be ascribed to the fact that tung oil contains primarily α-eleostearic acid and isomerized tung oil contains the β-acid. In addition, dehydrated castor oil, which reacts readily with styrene, probably contains some cis-cis-9,11-octadecadienoic acid (8) that may readily copolymerize with styrene whereas many isomerized oils probably have a predominance of cis-trans isomers (9).

Hewitt, *et al.* emphasized the importance of the viscosity of an oil in obtaining homogeneous copolymers with styrene, viz., that the oil should be prebodied to some extent before being allowed to react with styrene. In our work we have substantiated this importance of viscosity although Peterson (10) and Rinse and Korf (14) obtained poor results with bodied oils. These differences may have been caused by variations in the reaction technique.

Hewitt and Armitage stated that the presence of conjugation in blown oils was probably the reason that homogeneous products were obtained. On the other hand, Peterson (10) proposed the hypothesis that oxidized oils react readily with styrene by initiating or terminating styrene chains by means of their peroxide or epoxide linkages. Our results are at variance with both of these proposals for we have found that a blown oil containing very little conjugation and low peroxide content gave clear reaction products.

Most investigators seem to be of the opinion that the so-called copolymerization of styrene and drying oils proceeds by a chain reaction of the free radical type. Rinse (13) however has postulated that the reaction occurs via a proton shift because the usual catalysts for a free radical type of reaction have little or no effect on the course of the reaction whereas certain ketonic compounds such as anthraquinone, which are proton acceptors, promote the reaction.

It is not clear just how the peroxide functions in the reaction. Peterson postulated that a peroxide catalyst acts as a modifying agent, causing a reduction of the molecular weight of the polystyrene chains and thereby promoting greater compatability among the various molecular species. Our data lends support to this proposal.

The question whether the styrene actually copolymerizes with the oils and to what extent has not been conclusively answered. Although increasing the viscosity of the oils leads to more homogeneous products, this could be the result of greater mutual solubility as well as a result of copolymerization. Brunner and Tucker (2) have presented evidence based on ultraviolet and infrared absorption data that no interpolymerization between styrene and dehydrated castor oil occurs but that copolymerization between styrene and tung oil does occur. Petit and Fournier (11) have shown that no true interpolymerization between styrene and linseed oil takes place, but that a small amount of a condensation product consisting of one mole of styrene per mole of linolenic acid is formed.

Summary

Data and properties of products obtained by polymerizing styrene in the presence of drying and semidrying oils have been presented. Evidence is given showing that conjugation in an oil or peroxide content are not of fundamental importance for obtaining homogeneous products. The increasing of the viscosity of the oils appears to lead to the formation of styrenated products of higher homogeneity.

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Reactions of Fatty Materials With Oxygen. IX.[1] Analytical Study of the Autoxidation of Methyl Oleate[2]

H. B. KNIGHT, JOSEPH E. COLEMAN, and DANIEL SWERN, Eastern Regional Research Laboratory,[3] Philadelphia, Pennsylvania

An investigation of the reliability of conventional analytical procedures for the quantitative determination of oxygen-containing functional groups likely to be encountered in autoxidation reactions was reported in an earlier paper (3), in which model compounds and mixtures of them were studied. In the absence of peroxide and oxirane groups, the analytical procedures were shown to be reliable. When peroxides were present, however, unusually high and non-reproducible values for carbonyl oxygen were obtained, and iodine and saponification numbers were often unreliable. Large proportions of oxirane compounds interfered with hydroxyl oxygen determination but peroxides did not interfere. The determination of acid number and peroxide and oxirane oxygen was reliable in the presence of all other functional groups investigated. Techniques were described for the accurate determination of functional groups when peroxide and oxirane groups were present. As a check on the reliability of the analytical methods finally employed, good agreement was noted between total oxygen determined by difference from carbon and hydrogen analyses and total oxygen obtained from the sum of the analyses for the various oxygen-containing functional groups.

In the present paper we are reporting an analytical study of the autoxidation of methyl oleate irradiated with ultraviolet at 35°, 70°, and 100°C., employing the improved analytical techniques described earlier (3). The effluent gases were not studied in view of the systematic study of them by Hamilton and Olcott (1).

Experimental

Starting Material. The preparation of the methyl oleate employed has already been reported (3).

Oxidation Procedure. The oxidation procedures were the same as described previously (2) except that, in the oxidations at 35° and 100°, the quartz reaction flask was immersed in a constant temperature bath. In the oxidation at 70° heat from the ultraviolet lamps was sufficient to maintain the temperature to within ± 3°. Approximately 700 g. of methyl oleate were oxidized. The samples removed for analytical study were stored in the dark at 0° to —20° until analyzed. During the oxidation the

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[1] The previous paper in this series is reference (2).

[2] Report of a study in which certain phases were carried on under the Research and Marketing Act of 1946.

[3] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.