tration to 50%. Extract both neutral oil and unsaponifiable with petroleum ether as in the method for the determination of unsaponifiables (see Unified International Methods).

SUPPLEMENT II_{14}

Determination of Neutral Fatty Material Mixed with Fatty Acids •

The solution of the fatty material in ethyl ether is passed through a column of aluminum oxide. All the neutral fatty material and the unsaponifiables pass through the column. The fatty acids are adsorbed. The neutral fats and the unsaponifiables are recovered.

Apparatus: A glass tube, approximately 1.8 cm. in diameter and 30 to 40 cm. long, is drawn at one end to a diameter of 0.6 cm. The tube is mounted vertically on a support, with the drawn out end at the bottom. Place a small plug of defatted cotton in the neck of the drawn out end to serve as a support of the column of alumina. Fill the column within 10 cm. of the top of the tube. This upper portion of the tube serves as a reservoir which is filled by means of a funnel. The cotton plug can be replaced by a fritted glass disk. The liquid passing through the column is received in a flask.

Aluminum Oxide: Aluminum oxide suitable for adsorption chromatographic analysis is used. It can be obtained from Savory and Moore Ltd. or from the British Drug House Ltd. in England. The oxide is previously colored blue with bromothymol blue in order to locate the position of the region of adsorption of the fatty acids on the column. In this region the blue turns yellow. The preparation is obtained by impregnating aluminum oxide with a 3% alcoholic solution of bromothymol blue. The excess liquid is removed by drainage. The powder is then spread out on a hot plate. The drying is terminated at about 100°C. Mix a sufficient quantity of this strongly colored oxide with colorless oxide to obtain a faint but distinct blue tint.

Method: Aluminum oxide so prepared is suspended in ethyl ether and poured into the tube with care, preferably with the aid of a funnel. The oxide distributes itself uniformly and is packed gently. The column should be about 20 cm. high. It is necessary that it be covered with solvent at all times so that the upper surface is not exposed to the air. Approximately one gram of the fatty material is accurately weighed and dissolved in 50 to 80 ml. of ether. When the ether which initially covers the alumina has been drained to about 3 cm. above the free surface of the column, the solution of fatty material is added and passes through the alumina. When the level of the solution is not more than 3 cm. above the free surface of the column, add in portions, preferably numerous, 150 c.c. of ether to wash the column. About 5 cm. at the lower end of the column of alumina must not have changed color at the end of the washings.

The ether solution is concentrated by distilling the major portion of the solvent and then drying and weighing to obtain the weight of neutral oil and unsaponifiable matter contained in the analytical sample. The aluminum oxide can be reactivated in a satisfactory manner after use by evaporating the solvent with which it is impregnated and heating at 500°C. for three hours. After several reactivations part of the alumina is powdered too fine for good percolation through a column. It can be separated from this part by screening on a 325-mesh sieve. The alumina retained on the sieve can then be re-used. Chloroform can be used as a solvent instead of ethyl ether.

Styrenated Drying Oils

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STYRENE, first isolated over 100 years ago, has now become a readily available industrial chemical. The synthetic rubber program made necessary by World War II involved styrene production on the order of 400 million pounds per year. While large quantities will be consumed in the synthetic rubber and plastics industries, it is evident that styrene will be available for other purposes. One interesting application of the compound has been in the production of styrenated drying oils.

There are many references in the literature to reactions of drying oils with unsaturated hydrocarbons, including styrene and other vinyl compounds. Some of these references are very old, and most of the proposed methods yielded heterogenous products. About 1930 the possible reactions of styrene with drying oils began to attract considerable attention. Polystyrene was already well known but had been demonstrated to have serious deficiencies as a coating material, principally poor adhesion, brittleness, and incompatibility with other ingredients.

One of the first methods proposed for reacting styrene with a drying oil comprised polymerization of an aqueous emulsion of styrene and tung oil with hydrogen peroxide as a catalyst (1); the products were similar to factice. The next development was the disclosure of methods for polymerizing styrene with film-forming materials (including drying oils) in the presence of inert solvents (2). This principle of reaction in solvents was extended in several British patents (3) to include copolymerization of styrene with partially polymerized oils, frosting drying oils (tung and oiticica), and dehydrated castor oil. The function of solvents was presumably to establish reaction control in order to obtain useful clear copolymers.

When copolymerizing in the presence of solvents, the residual styrene odor was found to be very pronounced, and further processing of copolymers was not possible without removing the bulk of the solvent. The possibility of reacting styrene with drying oils by the mass or bulk polymerization method was in-

TABLE I

Styrenated Oil Formulations

No.	% Styrene[1]	Oil	Catalyst Added (based on wt. styrene)	Procedure -Hours at:					Total Hours
				160°C.[2]	160-250°C.	250°C.	250-300°C.	300°C.	
S-1	45	Alkali Refined Linseed	3% Benzoyl Peroxide	6	5	6	3	1	21
S-2	45	Alkali Refined Soybean	3% Benzoyl Peroxide	6	5	6	3	1	21
S-3	45	90% Alk. Ref. Linseed, 10% Tung	3% Benzoyl Peroxide	6	5	6	3	1	21
S-4	45	80% Alk. Ref. Soybean, 20% Tung	3% Benzoyl Peroxide	6	5	6	3	1	21
S-5	45	Dehydrated Castor (G-H Visc.)	3% Benzoyl Peroxide	6	5	6	1.5	....	18.5
S-6	45	Commercial Oxidized Linseed (Z3 Visc.)	None	....	24 hours 125°C.				24
S-7	45	Commercial Oxidized Soybean (Z3 Visc.)	None	....	24 hours 125°C.				24
S-8	45	Oxidized Dehydrated Castor (Z2 Visc.)	None	....	24 hours 125°C.				24

[1] Seven parts styrene and three parts alpha-methyl styrene.
[2] Styrene added over this period.

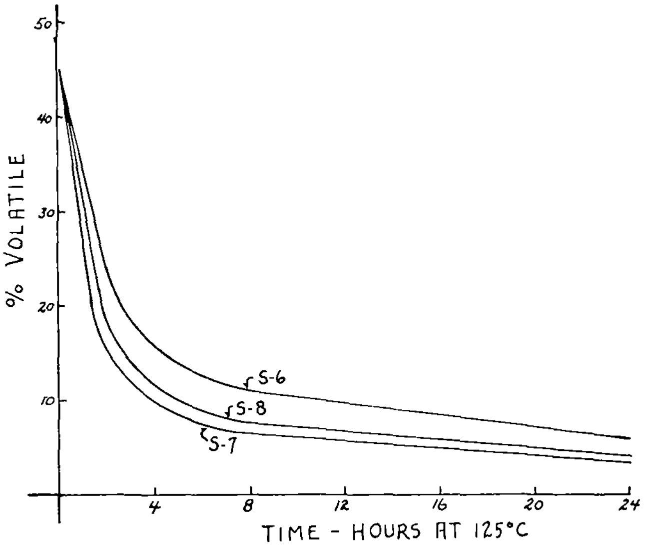

FIG. 1. Per cent volatile vs. time.

vestigated since it would offer certain advantages. A method has been described for preparing a linoleum cement by mass copolymerization of styrene with oxidized drying oils (4); in contrast to coating materials the copolymer was characterized as toluene insoluble.

One of the main difficulties in mass copolymerization of styrene with drying oils is to avoid the formation of heterogenous products. The use of alpha-methylstyrene in combination with styrene has been disclosed to render a successful method for obtaining styrenated drying oils (5). In the publication cited several formulations are given for styrenating both raw and oxidized drying oils of various types; the procedures and variables involved are discussed at length and need not be set forth here. However, several of the products have been prepared in accordance with the suggested methods and will be used herein as a basis for indicating the general characteristics of styrenated drying oils. In Table I the various procedures employed are summarized while Tables II and III give the analytical and evaluation data on the products obtained.

The reaction appears to be rapid in the early stages as judged by the disappearance of styrene monomer; it proceeds rather slowly after the first 2 or 3 hours. Data for runs S-6, S-7, and S-8, in which the styrene was added before applying heat, are shown graphically in Figure 1.

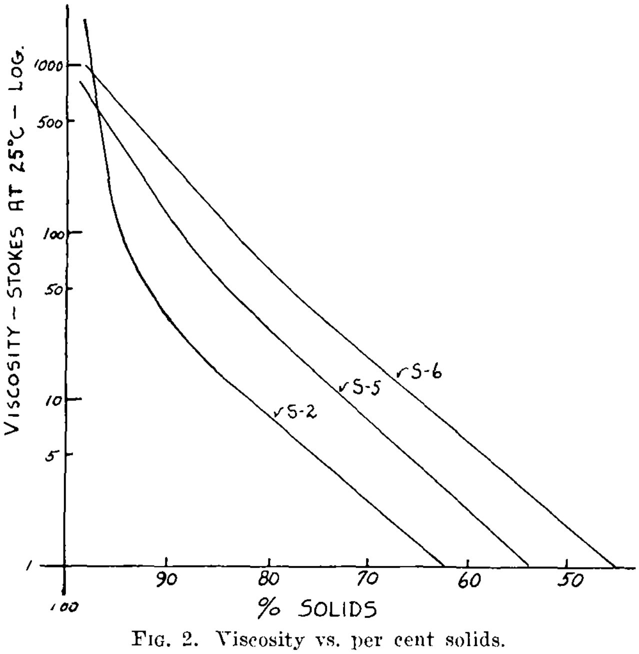

FIG. 2. Viscosity vs. per cent solids.

Colors of styrene-drying oil copolymers are generally very light. The copolymers and films therefrom appear even lighter than the Gardner color ratings would indicate. The products are all highly viscous oils or semi-solid resinous materials. Viscosity reduction curves are shown in Figure 2 for the soybean and dehydrated castor oil copolymers (S-2 and S-5) and the oxidized linseed copolymer (S-6). Although originally much more viscous, the ordinary soybean

TABLE II

Product Data

No.	Oil	% Volatile	Viscosity	Color (Gardner)	Film	Iodine Number	Saponification Number	Acid Number	Specific Gravity 15.5/15.5°C.
S-1	Linseed	3.0	44 min.[1]	8+	Clear	65.0	99.7	8.7	1.022
S-2	Soybean	4.0	Semi-solid	Opaque	Opaque	59.3	102.0	8.5	1.009
S-3	90% Linseed, 10% Tung	3.3	48 min.[1]	8+	Clear	68.2	101.0	8.4	1.017
S-4	80% Soybean, 20% Tung	4.3	Z9—	9—	Clear	60.8	103.0	7.8	1.007
S-5	D. C. O.	4.6	100 min.[1]	8+	Clear	67.2	100.2	9.3	1.009
S-6	Oxidized Linseed	6.7	108 min.[1]	15—	Clear	84.8	111.5	5.1	1.029
S-7	Oxidized Soybean	3.5	Semi-solid	11 (slightly hazy)	Clear	60.5	105.5	4.8	1.02
S-8	Oxidized D. C. O.	4.0	Semi-solid	11 (slightly hazy)	Clear	71.0	103.0	3.9	1.02

[1] Minutes at 25°C. in Gardner-Holdt tube.

TABLE III

Product Evaluation

No.	Oil	Drying Times (Hrs.)			Pencil Hardness (1 week)	Water Resistance (24 hrs.)	Alkali Resistance 1% NaOH (Hrs. fail)	Solvent Resistance (Mineral Spirits)
		Set-to-touch	Dry	Zapon Tack-Free (200 gms.)				
S-1	Linseed	2	20	104	4 B	Hazy	< 1	5 min.
S-2	Soybean	3	> 1 week	> 1 week	< 6 B	Opaque	1½	1 min.
S-3	90% Linseed, 10% Tung	2½	20	96	4 B	Sl. hazy	< 1	40 min.
S-4	80% Soybean, 20% Tung	2½	104	> 1 week	6 B	Opaque	< 1	5 min.
S-5	D. C. O.	1	8	102	4 B	Hazy	1	4 days
S-6	Oxidized Linseed	½	5	8	4 B	Sl. hazy	3	> 1 week
S-7	Oxidized Soybean	< ½	2½	2¾	6 B	Hazy	2	4 days
S-8	Oxidized D. C. O.	< ½	1½	2	3 B	Unaffected	> 5	> 1 week

oil copolymer breaks rapidly in viscosity when reduced with aromatic mineral spirits. The dehydrated castor oil copolymer is intermediate while the oxidized oil copolymer breaks least in viscosity with added spirits.

An examination of Table III will show that the properties of styrenated oils vary over a wide range, in this case with the type of oil employed. The products are comparable to those of oleoresinous varnishes and alkyd resins where the copolymerization is carried out with oils known to contain relatively large amounts of conjugated systems. Very fast set and hard-dry times can be obtained, also excellent water and alkali resistance. No difficulty is experienced in preparing homogenous products yielding brilliant clear films, except with ordinary soybean oil; inclusion of small amounts of tung oil obviates this difficulty. Solvent resistance for the products tabulated herein ranges from poor to good, again correlating with conjugated system content. Styrenated oils have in general very limited compatibility with bodied oils, etc.; this might be expected from the nature of the copolymers, as discussed later. While the data presented here can be taken as an indication of the characteristics of styrenated oils the whole range of properties is by no means encompassed; commercially styrenated oils of improved characteristics are now available.

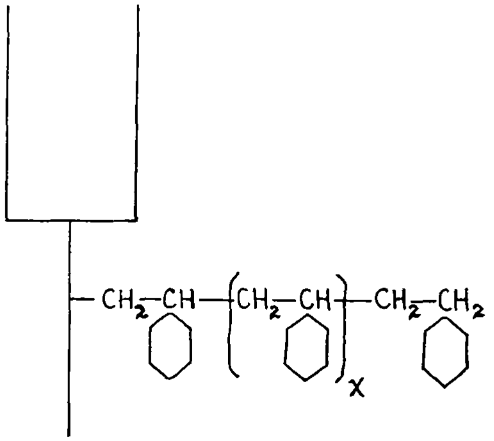

Fig. 3. Possible copolymer of styrene with non-conjugated oil.

Theoretical

Present theories as to the reactions involved in the copolymerization of styrene with drying oils have been necessarily developed mostly by empirical methods. The study of copolymerization, chain transfer and propagation, etc., is exceedingly difficult where one of the phases is a mixed natural ester such as a drying oil.

Three fundamental mechanisms have been proposed for the copolymerization of styrene and drying oils, depending on the nature of the drying oil phase of the system. It is thought that the mechanisms are basically similar for two or three component systems, but it must be recognized that important differences can arise where conditions are different, i.e., presence or absence of solvents and catalysts, temperature, etc. With this qualification, the following remarks may be taken as representing the present state of knowledge concerning the chemistry of styrenated oils.

Hewitt and Armitage (6) proposed a chain-transfer mechanism in the reaction with non-conjugated oils, leading to copolymers of the type illustrated in Figure 3. In this case the relatively labile hydrogen atoms on the C-8 and C-12 of the fatty acid radical are considered effective for chain transfer. The process is comparable to but proceeds more readily than chain transfer with an inert solvent. It was further suggested that heterogeneity in a two-component system might arise from the possible wide range of molecular weights of such products.

For conjugated drying oils the same authors suggested that copolymerization involves propagation of styrene chains across conjugated linkages as in the well known styrene-butadiene reaction; in this instance the conjugated fatty acid radical is considered a substituted butadiene (Figure 4). Initiation and termination of chains could, of course, occur by means of solvent and catalyst fragments where present. When initiation or termination as well as propagation occurred by means of conjugated fatty acid radicals, the effect would be to cross-link these radicals as shown in Figure 5. Gelation of styrene-tung oil systems occurs readily at temperatures far below those necessary for reaction between fatty acid radicals; cross-linkage to result in three-dimensional polymers seems certain where a high degree of conjugation is present. To explain the fact that small amounts of diene conjugation are sufficient to insure homogenous reaction, it is postulated that under

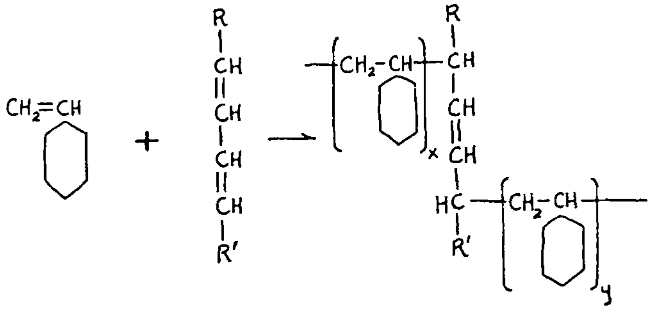

Fig. 4. Propagation of styrene chain across a conjugated diene.

given conditions a styrene chain will be propagated across conjugated linkages more readily than chain transfer will occur by non-conjugated radicals. It should be kept in mind that a relatively small amount of cross-linking would be sufficient to cause gelation. Therefore the predominant type of copolymer in this case is probably that consisting of a styrene chain propagated across a conjugated fatty acid radical but initiated by a solvent or catalyst fragment.

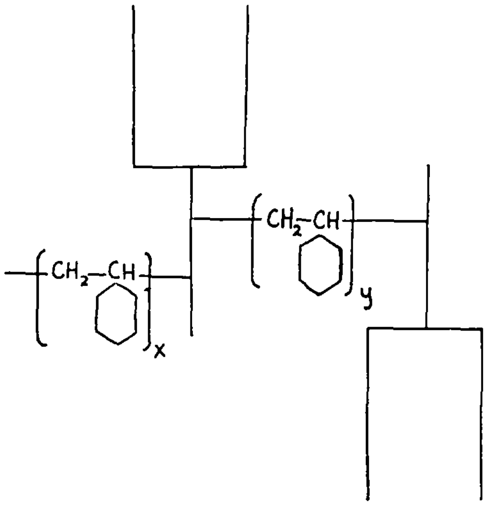

FIG. 5. Possible cross-linking by a styrene chain.

The third mechanism is that involved for styrene-oxidized oil copolymers. The similarity of this reaction to that involving conjugated drying oils was pointed out by Hewitt and Armitage, in view of the increase in diene content known to result from the oxidation of oils (7). This would explain the fact that homogenous products are obtainable, as in the case of the conjugated oils. However, the analogy is not useful in explaining the loss of oxidized oil character when such oils are styrenated. Accordingly, it has been stated that the mechanisms previously proposed do not apply to systems involving oxidized oils (8). Rather, it is believed that peroxide and similar linkages are ruptured and then serve to initiate and terminate styrene chains, resulting in oxygen linkages. The disappearance of oxidized oil characteristics could be accounted for by conversion of the unstable oxygen groups (ordinarily giving rise to color reactions, etc., when oxidized oils are heated) to stable ether linkages and similar groupings. Since the nature of the oxy-compounds and possible reactions of oxidized oils is highly complex, determining the exact character of their styrene copolymers is a difficult problem. A cyclic peroxide might initiate two styrene chains or propagate a chain across the fatty acid radical, resulting in copolymers as shown in Figure 6. Copolymerization reactions of this type would be similar to those involving natural conjugated oils in that some degree of cross-linkage might occur; they are less likely to lead to gelation, but the products are very viscous and sometimes rubbery in nature.

In an attempt to draw some conclusions as to the nature of the copolymers obtained from styrene-oxidized oil systems as compared to styrene-raw oil systems, the corresponding acids were obtained and examined. Data for the fractionation of fatty acids from S-1 (styrenated linseed) and S-6 (styrenated oxidized linseed) are shown in Table IV. The acids were obtained by saponification and subsequently fractionated by repeated precipitation from benzene solution with absolute methanol. In each case the high molecular weight acids are brittle resins and range downward to viscous liquids for the last (low molecular weight) fractions. The fatty acids in the high molecular weight fraction (No. 1) from styrenated linseed oil are opaque and somewhat crystalline on cooling whereas those from the styrenated oxidized linseed are clear. Cryoscopic molecular weights (in camphor) indicate that the equivalent weight of the styrenated oxidized linseed fatty acids gives approximately the true average molecular weight; for example, the cryoscopic M. W. is 2,450 as against an equivalent weight of 2,195 for the high molecular weight fraction of S-6. However, for the styrenated raw linseed the cryoscopic M. W. is only 1,930 as against an equivalent weight of 5,250 for the high molecular weight fraction.

TABLE IV

No.	Fraction	Wt. %	Acid No.	Equivalent Wt.
S-1 Acids	1	20.1	11.7	5250
S-1 Acids	2	32.2	16.0	3510
S-1 Acids	3	11.9	30.2	1860
S-1 Acids	4	35.8	88.0	637
S-6 Acids	1	32.8	25.6	2195
S-6 Acids	2	12.0	37.2	1510
S-6 Acids	3	7.2	51.2	1093
S-6 Acids	4	48.0	137.0	410

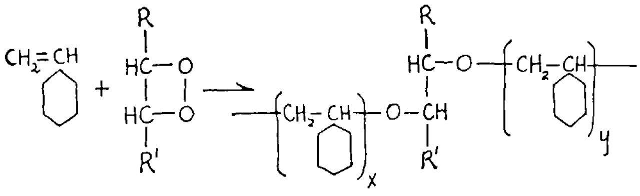

FIG. 6. Possible copolymer of styrene and cyclic peroxide.

This latter discrepancy is believed to indicate that styrenated non-conjugated oils contain polystyrene to a considerable degree, but all attempts to separate it from either the oils or the corresponding acids have been fruitless. A further indication of the probable presence of polystyrene may be found in the fact that styrenated raw linseed will develop incompatibility on continued heating, about 300°C., whereas styrenated oxidized oils do not. This would mean that true copolymers of the type shown in Figure 3 may form only a minor part of styrenated raw oils and that they represent mixtures of polystyrene, true copolymers, and unreacted triglycerides. The fact that equivalent weights are confirmed by cryoscopic molecular weights for the fatty acids from styrenated conjugated and oxidized oils indicates their homogeneity.

Styrenated drying oils of various types offer a new class of coating materials. Outstanding among the properties of certain of this class are fast set time, hard and impervious films, and excellent water and alkali resistance. The variance in properties among the types of styrenated oils can to some extent be explained in the light of present knowledge concerning the possible reactions and the nature of their products.

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Drying Oils From 2,2,6,6-Tetramethylolcyclohexanol and Linseed Fatty Acids[1,2]

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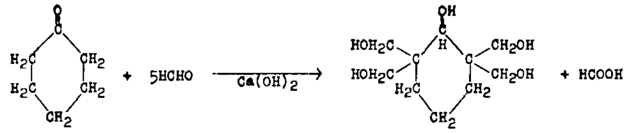
THE value of employing polyhydric alcohols with a functionality higher than that of glycerol for the preparation of reconstituted drying oils has been demonstrated by several investigators. Thus Burrell (2, 3) has described drying oil fatty acid esters of pentaerythritol and the polypentaerythritols, whereas Brandner and co-workers (1) have described similar esters of sorbitol. This paper describes a) a study of the esterification of 2,2,6,6-tetramethylolcyclohexanol (TMC) with linseed fatty acids, and b) the properties of the reconstituted oils.

TMC is a pentahydric alcohol with four hydroxyl groups which are primary and one which is secondary. It was first described in 1923 by Mannich and Brose (6), who prepared it by the condensation of the cyclic ketone, cyclohexanone, with formaldehyde in the presence of lime.



The pure material which melts at 131°C. is a white, beautifully crystalline solid with a hydroxyl content of 38.6%. The product used in the following investigations was prepared in the laboratory. It was technical in nature, possessing a hydroxyl content of 36.0 ± 0.5%. The pentaerythritol employed for comparative purposes was a commercial product known as "Pentek," which has a hydroxyl content of 47.0 ± 0.5% as compared to the theoretical value of 50.0%. The glycerol used was a redistilled U.S.P. reagent with a theoretical hydroxyl content of 55.3%. The linseed acids used were a commercial grade of distilled fatty acids.

The metallic stearates employed as esterification catalysts were prepared by the following procedure: a hot solution of pure stearic acid (6 g.) in alcohol (75 cc., 95%) was neutralized to phenolphthalein with alcoholic sodium hydroxide (0.2 N). The solution was diluted with hot water to a volume of 450 cc., and this was added with vigorous stirring to a 10% excess of the requisite metallic acetate in water (90 cc.). The precipitate was allowed to stand for one hour and then was filtered by gravity and washed with water (500 cc.). The paper containing the precipitate was then placed on a Büchner funnel, suction was applied, and the product was washed with small quantities of alcohol and ether. The soaps were finally dried *in vacuo* at 70°C.

Esterification of TMC

All reactions were carried out azeotropically in a one-liter, three-necked, round bottom flask, equipped with standard taper joints and modified to include a thermometer well. The flask was heated by a "Glas-Col" heating mantle. One neck of the flask was equipped with a stirrer whereas a second neck contained a water trap of the Dean and Stark (4) type, in which was inserted a Claisen-type tube. In one neck of the Claisen head was placed a condenser and in the other a small dropping funnel. The third neck contained a standard taper joint, into which was sealed a U-shaped tube with an outside diameter of about one-fourth inch. One end of the tube reached below the surface of the reaction mixture and the other contained a stopcock. This tube provided a convenient means of sampling, for the application of a positive pressure of nitrogen in a balloon at the condenser outlet forced a sample of the reaction mixture out of the open stopcock of the U-tube.

A xylene azeotrope was found to facilitate the esterification, the water of reaction separating in the Dean and Stark trap, whereas the xylene flowed back into the reaction vessel. The temperature depended upon three factors: the temperature of the "Glas-Col" heating mantle, the rate of stirring, and the amount of xylene in the reaction mixture. By keeping the first two factors constant, the temperature of the reaction was relatively easily controlled by the third means. The regulation of temperature by control of the amount of solvent has been described in some detail by Earhart and Rabin (5). Xylene could be added to the reaction mixture through the above-mentioned dropping funnel, whereas it could be removed through the water trap. By this means it was possible, with some degree of experience, to maintain a temperature constant within ± 1°. The xylene had an added advantage in that it provided an inert atmosphere for the reaction. Ordinarily 50 cc. of xylene was used at the start, a portion of which was allowed to fill the trap. The amount of xylene was adjusted by the above-indicated method as the reaction progressed.

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[1] Paper No. 96, Journal Series, Research Laboratories, General Mills, Inc.

[2] Presented at 22nd annual fall meeting, American Oil Chemists' Society, New York City, Nov. 15-17, 1948.