of the plant plasticized and Emulsorator plasticized samples was determined by the Scoco needle penetration method as described by Royce and Haskell (8). The consistency and over-all shortening quality of the Emulsorator plasticized samples are quite comparable to the plant plasticized samples.

Referring to Table 1, Sample S-17, a retail, household emulsifier type of vegetable shortening was Emulsorator-plasticized at an output of 45 lbs. per hour, with a 30°F. chilling unit jacket; temperature of the shortening from the chilling and texturating units was 55° and 73°F., respectively, and chilling and texturating unit agitator speeds were 330 and 770 r.p.m., respectively. This sample had an icing specific gravity at 30 min. of 0.49, which is equal to plant plasticized control sample S-1, a plastic range superior to the control and whiteness equal to the control. Sample Q-2, an emulsifier type of baker's vegetable shortening, was Emulsorator-plasticized at an output of 59 lbs. per hour, with a 40°F. chilling unit jacket; temperature of the shortening from the chilling and texturating units was 64° and 76°F., respectively; and chilling and texturating unit agitator speeds were 750 and 1170 r.p.m., respectively. This sample had an icing specific gravity at 30 min. of 0.57, which is slightly better than the plant plasticized control sample Q-1, a plastic range better than the control, and slightly inferior whiteness.

Sample QO-9, an emulsifier type of baker's meat fat shortening, was Emulsorator-plasticized at an output of 28 lbs. per hour, with a 20°F. chilling unit jacket; temperature of the shortening from the chilling and texturating units was 64° and 89°F., respectively; and chilling and texturating unit agitator speeds were 1150 and 1170 r.p.m., respectively. This sample had an icing specific gravity at 30 min. of 0.69, which is considerably better than the plant plasticized control sample QO-1, and a plastic range and whiteness comparable to the control.

The Emulsorator has also been used for plasticizing various fat bases containing a relatively high percentage of liquid vegetable oils.

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The Catalyzed Condensation of Phenol with Stearone and Methyl Heptadecyl Ketone[1]

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The condensation of phenol with stearone and methylheptadecyl ketone has been studied. The bisphenols and other products thus produced were identified by hydroxyl equivalent, molecular weight, infrared spectra, elemental analysis, and preparation of characteristic derivatives.

The commercial potential of this family of fatty derivatives was examined briefly from two approaches. Polymerization with formaldehyde, epichlorohydrin, and phosgene was investigated, and several fluids were prepared and screened as potential high-temperature lubricants.

OUR WORK (1) on the utilization of inedible animal fats as intermediates for commercially valuable materials suggested that bis-(hydroxyphenyl)alkanes derived from the condensation of phenol with ketones from C_{16} and C_{18} fatty acids would be worthy of investigation. Compounds of this type which are commonly referred to as bisphenols find use (2) as antioxidants, germicidal, bactericidal or teniacidal agents, pharmaceuticals, surface-active agents, fungicides, pesticides, and for the preparation of resins. They can be reacted with formaldehyde to give phenolic-formaldehyde resins (2); epichlorohydrin and caustic (2) to give polyepoxide resins; and phosgene or carbonate ester (3,5) to give a heat-resistant, dimensionally stable, thermoplastic polycarbonate.

Large-molecular-weight ketones have been prepared from saturated fatty acids and are commercially available. The use of dialkyl ketones in the preparation of bis-(hydroxyphenyl)alkanes from phenol has been reported by many investigators. They have not employed ketones of such high molecular weight as those derived from fats.

Liebnitz and Nauman (4) have reviewed much of the early patent literature and have given details as to the best procedures for the reaction of the lower dialkyl ketones with phenol. In general, our results agree quite well with their findings. They are:

1. Low temperatures, 25°–60°C., are more desirable and result in higher yields of the bisphenols than when temperatures in excess of 100°C. are used.
2. Sulfur and ionizable sulfur compounds containing a sulfur atom of apparent valence not greater than two promote the condensation of phenol with ketones. Anhydrous hydrogen sulfide was very satisfactory and has been the only sulfur catalyst employed by us.
3. Various acid-acting condensing agents, such as hydrochloric acid or a salt giving hydrochloric acid when reacted with water, are the most widely used. We have found that anhydrous hydrogen bromide or mixtures of anhydrous hydrogen bromide and anhydrous hydrogen chloride work very satisfactorily.

The ratio of reactant phenol to ketone can be varied; however when the ketones are solids, it has been advisable to use a large excess of phenol in order to maintain a liquid reaction mixture at low temperatures. Yet, even under the most favorable reaction conditions known, such reactions to produce

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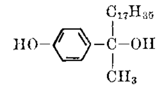
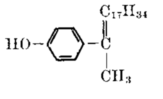
bisphenols are time-consuming. Our average reaction time was 20 hrs.

Separation of reaction products represented a difficult problem. Purification procedures used with low-molecular-weight dialkyl ketone condensates of phenol were not satisfactory. With low-molecular-weight ketones, gentle heating under vacuum was sufficient to remove unreacted starting materials, but with such ketones as those derived from fat much stronger heating was required and complete separation was not possible without effective fractional distillation. The solubility of the ketones and reaction products was also similar enough so that separation by selective recrystallization was not feasible. Complete separation and purification of the reaction products were best accomplished by repeated vacuum distillations and then by several successive recrystallizations from Skellysolve B or 95% of ethanol.

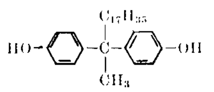
Some of the possible products formed during the condensation of phenol with methyl heptadecyl ketone are the following:



I
OH eq. 188

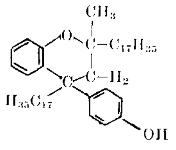


II
OH eq. 359

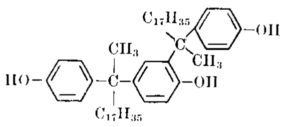


III

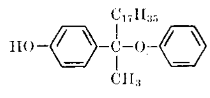
P,P'
P,O' } OH eq. 226
O,O'



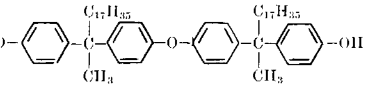
IV
OH eq. 717



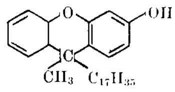
V
OH eq. 270



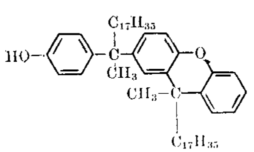
VI
OH eq. 453



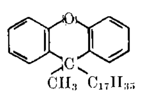
VII
OH eq. 444



VIII
OH eq. 453



IX
OH eq. 793



X

A typical condensation of methyl heptadecyl ketone with phenol resulted in three main fractions. These were a) an olefin, Structure II, 2-(4-hydroxyphenyl)-2-nonadecene, which was probably formed through the dehydration of a tertiary alcohol intermediate; b) the desired bisphenol, Structure III, 2,2-bis(4-hydroxyphenyl)nonadecane; and c) a high-boiling liquid fraction proposed from infrared analysis and hydroxyl equivalent to be a dimer of the bisphenol, Structure VII. The yields of these fractions varied with the temperatures that were employed. The use of temperatures of 120°C. or higher resulted in approximately 50% yields of the olefin, and 50% of a high-boiling fraction that was liquid could not be recrystallized or vacuum-distilled. This high-boiling fraction has not been identified. Attempts to prepare a solid deriative were not successful. Its proposed structure is that of chroman, Structure IV. Hydroxyl equivalent found, 767; theory for chroman structure, 717. Controlling the temperature to 45°–65°C. resulted in a much cleaner reaction mixture. Of the compounds separated, the olefin represented approximately 50%, the bisphenol 20%, and the dimer 10%. Qualitative tests for carbonyl function in reaction mixtures, accomplished both by infrared analysis and 2,4-dinitrophenyl-hydrazine reagent, indicated near quantitative reaction of the carbonyl function.

The physical characteristics of these compounds, low melting and high boiling, would tend to suggest their use in the preparation of high-temperature, thermally stable lubricants. Various derivatives were prepared from the phenol ketone condensation products, and from these derivatives the parent compounds were further characterized and in several instances their thermal stability was determined.

The thermal stability tests were run in glass apparatus under a blanket of nitrogen with heating periods of 10 hrs. at temperatures of 690°F. The procedure followed that outlined in the Wright Air Development Center Technical Report 54-532, catalogued by ASTIA as AD 65414. The thermal stability tests were conducted on the following compounds: a) 2,2-bis(4-acetoxyphenyl)nonadecane; b) 4,4'-bis[2-(4-acetoxyphenyl)-2-nonadecyl]diphenyl ether; and c) 2,2-bis(4-phenoxyphenyl)nonadecane. Compounds b) and c) above are liquids and also showed the greatest thermal stability, 3.6 and 4.6% weight loss, respectively. Compound a) is a solid, melting at 63.5–64.5°C. It lost 6.9% weight in the thermal stability test. The thermal stability of organic acid esters is, in general, poor as compared with tertiary amines, phenyl ethers, or inorganics such as the silicones, and exceptional thermal stability was not expected from the compounds tested. Investigation of decomposition fragments indicated that the structure of the bisphenol was fairly stable and worthy of more complete investigation.

A preliminary investigation of the polymerization of the bisphenols was also made. The crude material after one fractional distillation was used in all of our polymerization studies and was probably the reason for not obtaining more desirable polymers. Formaldehyde condensation with acid and alkaline catalysts was attempted with the bisphenols from stearone and methylheptadecyl ketone designated as bisphenol "S" and bisphenol "MH." Polycarbonates and polyepoxide resin formations were attempted on the bisphenol of stearone. The formation of resins of bisphenol "MH" appears to be more promising than those from bisphenol "S." Consideration of the crude material and polymerized reaction mixture indicates that desirable commercial polymers could possibly be produced from this family of fatty compounds. Purification of the starting material is required to improve the hardness and durability of the resins. Also their use as raw materials for polycarbonates and polyepoxide formations should result in some very interesting polymers.

The new compounds were characterized by determination of hydroxyl equivalents, using the method of Freed and Wynne (6), carbon-hydrogen analyses, infrared absorption spectra obtained with a Beckman IR-4 infrared spectrophotometer, preparation of derivatives and evaluation of the derivative properties such as saponification equivalent, carbon-hydrogen analysis, index of refraction, density, and molar refraction where applicable.

Experimental

I. Condensation of Phenol with Methyl Heptadecyl Ketone

Low Temperatures. A mixture of 4 moles of ketone to 16 moles of phenol was heated until solution resulted. At a temperature of 40°C. hydrogen sulfide was added until saturation was reached. After addition of the catalyst, anhydrous hydrogen chloride was added for ½ hr., then the addition of anhydrous hydrogen bromide was started. On the addition of hydrogen bromide, crystallization began and the temperature rose spontaneously to 65°C. The reaction mixture was cooled in a cold-water bath to 45°C. and maintained there for a period of 10 hrs. Unreacted phenol, hydrogen sulfide, hydrogen chloride, and hydrogen bromide were removed by washing with water and filtering the reaction mixture. The reaction mixture was distilled into five fractions. These fractions were redistilled, and the center cuts were recrystallized from Skelly B.

The following compounds were isolated and identified:

a) 2-(4-Hydroxyphenyl)-2-nonadecene, II, b.p. 230-232°C./0.1 mm.; m.p. 67–69°C.; hydroxy equivalent found, average of six determinations, 359; theory, 359. Anal. Calcd. for $C_{25}H_{42}O$: C, 83.5; H, 12.05. Found: C, 83.6; H, 12.02.

This compound is a white waxy solid. It is formed from the dehydration of a tertiary alcohol, an intermediate in the formation of the bisphenol compound, and represents approximately 50% of the products isolated.

b) 2,2-Bis(4-hydroxyphenyl)nonadecane, III, b.p. 268–271°C./0.1 mm.; m.p. 80–81.5°C.; hydroxy equivalent found, 239; theory, 226. Anal. Calcd. for $C_{31}H_{48}O_2$: C, 82.2; H, 10.7. Found: C, 81.95; H, 10.47.

This compound is a white crystalline solid and represents approximately 20% of the total products isolated. This compound was further purified in a later experiment by acetylation, distillation of acetate, saponification of ester, and recrystallizations from 95% ethanol and Skelly B to give a product m.p. 85.5–86.5°C.; hydroxyl equivalent found, 229; theory, 226.

c) 4,4′-Bis[2-(4-hydroxyphenyl)-2-nonadecyl]diphenyl ether, VII. This compound is a dimer formed during preparation and isolation of the bisphenol compound. It is a dark viscous oil at room temperature, obtained by distillation at 290–300°C./0.3 mm. and represents approximately 10% of the total products isolated. This material was redistilled twice and the center cut was used for the preparation of derivatives to be described later. Hydroxyl equivalent found, 436; theory, 444. Anal. Calcd. for $C_{62}H_{94}O_3$: C, 83.8; H, 10.65. Found: C, 83.92; H, 11.03.

High Temperatures. An increase in the temperature was considered as a means of removing water formed in the reaction and thus increasing the yield of the bisphenol fraction. The procedure was similar to the above experiment. Two moles of ketone were mixed with eight moles of phenol and heated until dissolved. Anhydrous hydrogen sulfide, hydrogen bromide, and hydrogen chloride were then added, and the temperature was increased to 120°C. After one and one-half days reaction had ceased, and nearly theoretical water of condensation had been collected. Excess phenol was removed by distillation at reduced pressure; some additional water was collected with the phenol. A qualitative test for ketone in the reaction mixture with 2,4-dinitrophenyl hydrazine reagent was negative, indicating complete reaction of the carbonyl group. A material balance indicated however that only 1 mole of phenol had condensed with 1 mole of ketone. Distillation of the reaction mixture resulted in two fractions, the olefin 2-(4-hydroxyphenyl)-2-nonadecene and a high boiling fraction that could not be distilled without decomposition. The high boiling fraction remained a liquid on cooling; efforts to recrystallize a solid from the residue were unsuccessful. Infrared analysis of the residue indicated hydroxyl groups and additional C–O bands not in the olefin in the 1,200 cm.$^{-1}$ region. These are probably due to ether formation or ring closure. The hydroxyl equivalent of the crude material was found to be 767; theory for a chroman structure (IV) is 717. Attempts to prepare a solid derivative that could be characterized were not successful.

II. Reaction of 2-(4-Hydroxyphenyl)-2-nonadecene

Acetylation. Ten grams of the recrystallized olefin were acetylated with 15% solution of acetic anhydride in pyridine. The stoichiometric amount plus 10% excess of the acetylating agent was used. The reaction mixture was raised to reflux temperatures and boiled for 10 min. The acetylated product was poured over ice, collected, and washed with water until neutral. The acetate was recrystallized twice from 95% ethanol and dried. The product rapidly decolorized aqueous potassium permanganate solution and bromine in carbon tetrachloride. Its melting point was determined as 49–50°C. Saponification equivalent was determined on the recrystallized sample. Found, 417; theory for acetate of 2-(4-hydroxyphenyl)-2-nonadecene is 402. Anal. Calcd. for $C_{27}H_{42}O_2$: C, 80.8; H, 11.06. Found, C, 80.65; H, 11.27.

III. Reactions of 2,2-Bis(4-hydroxyphenyl)nonadecane

Acetylation. The hydroxyl content of a large batch of crude bisphenol was determined, and the stoichiometric quantity plus 10% excess of acetic anhydride in pyridine was added to acetylate the hydroxyl groups. The mixture was refluxed for 2 hrs., washed with water, then with dilute HCl, and again with water until neutral. The oily organic layer was separated and distilled under reduced pressure. The pre-cut was mostly phenyl acetate. The diacetate was difficult to distill without decomposition, but by rapid heating a relatively pure fraction, boiling at 296–297°C./0.8 mm., was obtained. The acetate was recrystallized until infrared analysis indicated the absence of hydroxyl groups. This required five recrystallizations, m.p., 63.5–64.5°C. Saponification equivalent found, 268, 265; theory, 268. Anal. Calcd. for $C_{35}H_{52}O_4$: C, 78.2; H, 9.75. Found: C, 77.9; H, 9.57.

Phenyl Ether Formation (Ullmann Reaction). 1. Fifty-six grams of recrystallized bisphenol "MH" were added to 9 g. of KOH in a 500-ml., round-bottom flask and allowed to react exothermically. When reaction was completed, the mixture was heated under reduced pressure for 3 hrs. at 150°C. in an oil bath to remove the water formed. At the end of this time 19.4 g. of phenyl bromide and 2 g. of copper powder catalyst were added, and the mixture was stirred for 1 hr. at 150°C. The temperature was then raised to 200°C. and held for 1 hr., when the reaction appeared complete.

The reaction mixture was dissolved in Skelly B, but attempts to filter the inorganic salt and copper catalyst were not successful. Attempts to wash with water resulted in emulsions. The Skelly B was evaporated, and the product was dissolved in ether. It was then possible to wash the ether solution with water until neutral. Distillation gave three main fractions. The first two fractions were mainly biphenyl. The high boiling oil, 10 g. boiling at 270–280°C./0.45 mm., was dark in color and impure. Infrared spectra showed a large hydroxyl absorption band. Further characterization was not attempted because of the low yield.

2. The following reactants were added to a 500-ml., round-bottom flask equipped with a stirrer, thermometer, and Podbielniak tube for separating immiscible liquids of different densities: 0.25 mole (113 g.) of recrystallized bisphenol "MH"; 157 g. or 110% excess of bromobenzene reactant used as a solvent for reaction mixture; 0.5 mole (69.1 g.) of K_2CO_3; 1 g. of Cu_2Cl_2 powder and 5 g. of dried activated copper powder.

The mixture was heated gently to reflux temperature, at which time the theoretical amount of water had been collected. Heating was continued for an additional hour with no more water obtained.

Attempts to filter the reaction mixture, using a filter aid, were not too successful. The filtered reaction mixture was distilled at reduced pressure; two fractions were obtained. Fraction 1 was a white waxy solid containing considerable hydroxyl groups as shown from infrared analysis. Fraction 2 was a yellow oil, b.p., 300°C./0.2 mm. It also contained hydroxyl groups, but it was possible to remove these by washing the mixture with a 5% alcoholic sodium hydroxide solution. Infrared analysis confirmed the removal of the hydroxyl groups. The following physical properties were determined on the oil: $n^{25/D}$, 1.528; $d^{25/25}$, 0.962; M_n found, 193.7; theory, 194.4. Anal. Calcd. for $C_{43}H_{56}O_2$: C, 85.4; H, 9.35. Found: C, 86.65; H, 10.45.

Dimethyl Ether Derivative. To 15 g. of purified bisphenol "MH" were added 4 g. of sodium hydroxide in 100 ml. of water. The mixture was stirred in a three-necked flask equipped with a dropping funnel, reflux condenser, and mechanical stirrer. The reaction mixture was cooled to 10°C., and 10 ml. of dimethyl sulfate were added slowly. After standing several days at room temperature, it was heated to reflux to destroy any unreacted dimethyl sulfate and then cooled. The solid was filtered off and washed with acid, then with water until neutral. The product was separated, dissolved in Skelly B, and dried over $CaCl_2$.

The Skelly B was evaporated on a steam bath, and the mixture was distilled. The main fraction boiled at 240–245°C./0.2 mm. This was a waxy cream-colored solid, melting over a wide range, 65–75°C. Infrared analysis of the product indicated a large amount of free hydroxyl groups. Attempts to wash out the phenolic products with alcoholic NaOH resulted in an emulsion that was difficult to break. Because of the low yield and low boiling point of the product further purification was not attempted.

Phenyl Urethan. The procedure of Shriner, Fuson, and Austin in "The Systematic Identification of Organic Compounds" was employed. The phenyl urethan obtained was purified by recrystallization from carbon tetrachloride, m.p. 81–83°C. A mixed melting point with starting material gave a melting point depression of 8°C. Anal. Calcd. for $C_{45}H_{58}N_2O_4$: C, 78.1; H, 8.39; N, 4.05. Found: C, 77.39; H, 8.28; N, 4.02.

IV. Reactions of 4,4-Bis[2-(4-hydroxyphenyl)-2-nonadecyl] diphenyl Ether, "Bisphenol 'MH' Dimer"

Acetylation. The preparation of the acetate of the dimer was similar to that described for the previously prepared acetates. A 15% solution of acetic anhydride in pyridine was refluxed with the dimer for ½ hr. The mixture was then poured into crushed ice, and the oil was separated. The oily layer was washed with water, hydrochloric acid, and water until neutral. The oil was distilled through a 6-in. Vigreaux column, the center cut was redistilled, and the following properties determined on this fraction: $n^{25/D}$, 1.4907; $d^{25/20}$, 0.920; M_n found, 315; theory, 300; m.p. 15–16°C.; b.p. 230°C./0.2 mm. Anal. Calcd. for $C_{66}H_{98}O_5$: C, 81.7; H, 10.18. Found: C, 81.95; H, 10.46.

Benzoylation. To 30 g. of dimer in pyridine were added 10 ml. of benzoyl chloride. After initial reaction the mixture was heated to reflux for 1 hr., cooled to room temperature, and washed with water to remove pyridine. After drying with calcium chloride over-night the product was vacuum-distilled. The main fraction was a low-melting, dark-colored solid distilling at 188–192°C./0.08 mm. Attempts to purify the solid by recrystallization were not successful.

Nonanate of Dimer. To 30 g. of dimer were added 10 ml. of nonanoyl chloride in a pyridine solution. After initial reaction the mixture was heated under reflux for 1 hr. The crude product was washed with water and dried over $CaCl_2$. The product was distilled under reduced pressure; two fractions were obtained. Fraction 1 was a low-melting solid which was recrystallized and tentatively identified as the monononanoate from the saponification equivalent. Fraction 2 was a dark fluid at room temperature, distilling at 196°C./0.07 mm. Because of the low boiling point of nonanate the thermal stability was not determined, and further characterization was not attempted.

V. Polymerization of Bisphenol from Methylheptadecyl Ketone

Formaldehyde with Acid Catalysts. Bisphenol "MH," 9.2 g. (0.02 mole), formaldehyde 2.9 g. (0.037 mole), oxalic acid, 0.04 g., and Aerosol OT, 0.02 g., were refluxed for 6 hrs. Water was removed under vacuum, and the melted resin was poured into two separate aluminum pans. Hexamethylene tetraamine was added to the resin and heated in an oven. The resins formed were very dark-colored and flexible. They were not however very tough.

Formaldehyde with Alkaline Catalyst. Bisphenol "MH," 9.1 g. (0.02 mole), formaldehyde, 6.5 g. (0.08 mole), and 0.5 g. of NaOH in 20% water solution were refluxed 6 hrs. The mixture was cooled to room temperature and neutralized with dilute citric acid.

The product was washed with water, then dehydrated under vacuum. Adding a glycerine phosphoric acid mixture to resin while warm resulted in nontacky polymer.

VI. Thermal Stability

The thermal stability tests were run in glass apparatus under a blanket of nitrogen with heating periods of 10 hrs. at temperatures of 690°F. (Refluxing Aroclor 1254 was used.)

The empty sample tube was weighed accurately, the lower bulb of the tube was half-filled and reweighed. The apparatus was assembled, using Apiezon T grease on the glass joints. The system was evacuated, and nitrogen was admitted alternately to remove all traces of air above the sample and refluxing liquid. A positive pressure of 10 mm. of Hg was maintained on the system by means of a nitrogen bubbler. Maximum heating was used to raise Aroclor 1254 to reflux temperature, then was adjusted to maintain the desired temperature of 690°F. Heating was maintained for 10 hrs., after which time the sample was cooled to room temperature. The sample tube was then removed, cleaned, and weighed; the collector tube was also weighed. The weight of sample loss and the weight of volatile decomposition products which were condensed in the collector tube were recorded. The data tests are shown in Table I. Analysis of fragments collected indicated they came from the terminal groups. It therefore appears that the basic structure of the bisphenol is thermally stable and a desirable intermediate in the preparation of high-temperature lubricants.

TABLE I
Thermal Stability Data

Compound	Wt. of sample (g.)	Wt. of condensable fragments (g.)	Total wt. loss (g.)	Temp. (°F.)	Wt. loss (%)
1. 4,4'Bis[2-(4-acetoxyphenyl) 2-nonadecyl]-diphenyl ether.	9.3372	0.1404	0.3362	690	3.6
2. 2,2-Bis(4-acetoxyphenyl)-nonadecane	9.5974	0.3698	0.6619	690	6.9
3. 2,2-Bis(4-phenoxyphenyl)-nonadecane	9.8593	0.2521	0.4521	690	4.6

VII. Condensation of Phenol with Stearone

The procedure was similar to that for condensation of phenol with methyl heptadecyl ketone. Anhydrous hydrogen sulfide was used as catalyst. The condensing agent was anhydrous hydrogen chloride and anhydrous hydrogen bromide. The ratio of phenol to ketone was 10 to 1, and the reaction temperature was 110–130°C.

To 127.5 g. of stearone (0.25 mole) were added 235.3 g. of phenol (2.5 moles), and the solution was heated to 130°C. Anhydrous hydrogen sulfide was added for 15 min. and anhydrous hydrogen bromide for 30 min. The reaction was heated with stirring at 110°C. for 15 hrs., after which time the tempereature was increased to 125°C. and anhydrous hydrogen bromide was added for an additional hour. Total reaction time was 21½ hrs. When reaction mixture had cooled to 70°C., 150 ml. of benzene were added, and the water formed in the condensation was removed by azeotropic distillation; 5.3 ml. of water was obtained, 12% more than theoretical.

Phenol and benzene were removed under reduced pressure, and the residue was distilled under vacuum, 80 g. (47% of theory) of product being collected at 295–300°C./0.6 mm. The low-boiling fraction constituted 9.5% by weight of theoretical yield, and the remainder was pot residue. Infrared analysis indicated a possible ether group in the pot residue. The solid distillate, m.p. 49–50°C., was recrystallized several times with Skelly B and 95% of ethanol with three main fractions resulting. These fractions were identified from hydroxyl values and infrared analysis as a) the olefin 18-(4-hydroxyphenyl)-18-pentatricontene, m.p. 68–70°C., b) the bisphenol 18,18-bis(4-hydroxyphenyl)pentatricontane, m.p. 77–78°C., and c) a dark red oil with a high hydroxyl equivalent. A qualitative test for stearone in the reaction product with 2,4-dinitrophenyl hydrazine reagent was negative. Stearone gives a hydrazone, m.p. 80–85°C., with the reagent.

VIII. Polymerization of the Bisphenols Obtained from Stearone

Formaldehyde with Acid Catalyst. Bisphenol "S," 3.5 g. (0.005 mole), and 0.4 g. (0.005 mole) of formalin were placed in a test tube and heated until the bisphenol melted. Then about 0.05 g. of oxalic acid and a small amount of Aerosol OT were introduced. The mixture was stirred and heated at 210°F. for about 2 hrs., then in an open flame intermittently for ½ hr. A rather sticky, fairly viscous product resulted.

The above procedure was repeated, using twice the amount of formaldehyde. A sticky, slightly viscous product resulted as before.

A similar experiment with bisphenol "S" and formaldehyde, using sulfuric acid as a catalyst, was attempted, but a viscous, dark, resinous product resulted.

Formaldehyde with Alkaline Catalyst. Bisphenol "S," 3.5 g., and 0.6 g. of formaldehyde were heated with concentrated ammonium hydroxide at 212°F. for 2 hrs. Two phases were present throughout the reaction period. Final heating was at 310°F. for approximately ½ hr. A dark amber, viscous product resulted.

The above procedure was repeated, using a dilute solution of sodium hydroxide as catalyst. A similar dark amber, viscous product resulted as before.

Copolymerization of Bisphenol "A" and Bisphenol "S" with Formaldehyde. A mixture of 0.045 mole (30.4 g.) bisphenol "S" and 0.05 mole of formaldehyde was heated with 0.5 g. of oxalic acid and Aerosol OT to reflux for 4 hrs. The bisphenol "A," 0.005 mole (1.15 g.), was added and the temperature was held at 165°F. for 4 hrs. Water was removed under vacuum; the mixture reached a temperature of 265°F. The product was dark reddish brown and viscous.

Polycarbonate Resin. Bisphenol "S," 0.05 mole (33.9 g.), and 0.5 mole of pyridine were mixed together at 25°C. Phosgene, 0.05 mole, dissolved in 50 ml. toluene was added by drops, causing a temperature rise to 45°C. during the addition.

The reaction was stirred for 1 hr. at room temperature. The pyridine was removed by washing with dilute acid, then with water until neutral. Toluene was removed on a steam bath. The product that resulted was a waxy semi-solid.

Epoxy Resin Preparation. A slurry of bisphenol "S," 0.1 mole (67.7 g.), in 20% sodium hydroxide solution was heated to 175–185°F. in a flask fitted with stirrer, condenser, thermometer, and dropping funnel. Epichlorohydrin, 9.25 g. (0.1 mole), was added by drops to the stirred mixture. The temperature was held at 175°–185°F. for 6 hrs., then dilute HCl was added until slightly acidic. Sodium chloride and excess HCl were removed by washing with water. The remaining water was removed under vacuum. The product was a yellow waxy material which would not cure to a hard resin when admixed with ethylene diamine, diethylene triamine, triethylene tetraamine, or phthalic anhydride at baking temperatures.

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A Determination of the Effects of Several Variables on the Performance Characteristics of Shortening, Using Statistical Experimental Designs

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To obtain shortening of higher water absorption, one should increase the level of monoglyceride used in the shortening. Icing volume is adversely affected by higher levels of monoglycerides. It is immaterial whether the monoglyceride has 40–44% or 56–58% *alpha* mono content, and the I.V. may range from 56 to 90 without producing significant effects on water absorption, icing volume, or cake results. Tempering and the choice of vegetable fat or rearranged meat fat stocks are of importance.

I. Statistical Experimental Design and Its Applications

THIS PAPER will present a simple outline of procedure used in a shortening study where experimentation was on a statistical basis to achieve maximum results in a minimum of experimental time.

While the use of statistical methods in production and quality control is widely accepted, we find that some of the statistical techniques available are not well known to the research and development chemist. It is hoped that this presentation will stimulate further investigation.

Much chemical experimentation has to deal with systems made up of a number of variables, in which the chemist has to determine the proper conditions for each variable necessary to achieve optimum results. One common way to do this would be to take one particular ingredient (or factor), vary it to find the level which works best, then hold that optimum condition fixed and vary some other factor: find its optimum, and go on to another variable. There are some cases however for which this is not the most efficient way to proceed.

Statistically it is possible to show that we can get more accurate results, in a shorter period of man-hours, by applying some of the theories of statistical experimental design. This is an orderly, planned experiment in which we have decided how to vary the factors we wish to study in relation to one another. Under this approach all variables are changed simultaneously instead of only one factor at a time.

The advantages of changing all variables simultaneously according to a definite plan as opposed to the "one-varying, others-fixed" approach can be summed up as follows. We are able to determine differences in end-results that are smaller than would be apparent if only one item were varied at a time. This approach brings to light the changes in end-results caused by the interaction of variables, a factor hidden if only one at a time were moving. The use of this approach enables one to make an accurate estimate of the inbred experimental error in our procedure, a factor difficult to determine in common procedures without running a number of separate repetitive experiments.

We can chart a typical chemical problem of four variables (Table I). By assuming that our final answer will be made up of some combination of the varying levels of use of this material, we can quickly determine the number of total runs required to conduct a complete factorial series. With one variable having four possible levels of use, two other variables each with three levels of use, and a fourth ingredient having only two levels of use, we would have 72 distinct experimental runs to perform.

TABLE I

A Factorial Experiment

Variables	Code	Levels for use	Total number of levels
Alpha mono in monoglyceride	A	40 48 56	3
Iodine value	B	50 70 90	3
Alpha mono in shortening	C	1.75 2.00 2.25 2.50	4
Tempering	D	Absent Present	2

It is satisfactory, in a majority of cases, to run just two levels of use for each of the four factors, the high limit and the low limit, for each of the four variables and, by graphical and mathematical means, to consolidate the data thus gained to fill in what we might not have derived directly from experimentation. Two-level experiments are simple to