

Report of the Literature Review Committee

Annual Review of the Literature on Fats, Oils, and Detergents. Part I.

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INTRODUCTION

This review of the 1961 literature was compiled from current, original publications and from abstracts of publications. A few salient points may be summarized. Recent growth of numerous industries has been based upon more intensive research on natural oils and fats. Many new possibilities for increased application of a range of fatty derivatives such as vinyl esters of fatty acids, newly developed fatty amides, monobasic and dibasic fatty acid anhydrides, epoxy acids, fatty acid ketene dimers, etc. are being investigated. Few subjects of nutritional research today are receiving so much attention, and are at such a critical turning point as those involving fats. There is also a flood of information in the biochemical and physiological fields. It is of particular interest to note that the techniques of gas-liquid chromatography and thin-layer chromatography have become invaluable techniques. Through their use, striking advances are being made in the chemistry and biochemistry of fats.

SOAPS, SURFACTANTS, AND DETERGENTS

Processes

MANUFACTURE

A review of soap manufacture discussed theory and practice (Wallis, *Research* [London] 14, 188-192). Patented were transparent soaps (Kelly and Hamilton, *U.S.* 2,970,116), and a shortened process for isolation of curd soap (Palmquist, *Swed.* 168,085). A pure soap of equal to or greater than 14C atoms was prepared by dry NaOH saponification followed by extraction with ethylene dichloride or isopropyl alcohol (Campbell, *Ger.* 1,049,523). The electrolyte content of soap was automatically controlled by viscosity measurement (Palmquist, *Soap, Perfumery & Cosmetics* 34, 353-357). The soap was constantly washed with a salt solution. The separated soap and salt solution were continuously removed. A portion of the salt solution was mixed with fresh alkaline salt solution and with the soap used for washing (Finsberg, *Ger.* 1,088,172). The acid alkali metal salts of bi- or multivalent acids were used to neutralize the separated soap and prevent separation (Palmquist, *Ger.* 1,033,826). A high fatty acid plasticized soap content was attained by adding a paraffin oxidation product (Postol'nyi and Lysenko, *U.S.S.R.* 131,852). Addition of an aqueous emulsion of a silicone during neutralization of vegetable oils permits separation of the soap stock (Gilles, *Fr.* 1,181,409).

Rapid addition of a metal salt solution gives improvement in the preparation of a fine-grained soap of multivalent metals (Meyer, *Ger.* 1,085,517). Aluminum soaps of predetermined particle size, agglomerating characteristics, and controlled composition are obtained by incremental aluminum salt addition (Bulloff, *U.S.* 2,957,934).

Formulations and a process for producing blue mottled soap are described (Milwidsky, *Soap Chem. Specialties*, 37, No. 5, 62-65, 139-140). A process for producing transparent soap is claimed (Kelly and Hamilton, *Ger.* 1,047,972). Soap compositions were stabilized by adding hydrazinium compounds (Fusco and Harshman, *U.S.* 2,971,917).

Purification of alkylbenzene sulfonates by treatment with ozone gave better color with improved odor (Krems and Gray, *U.S.* 2,962,526), while hydrogen peroxide proved useful for bleaching of crude fatty amide mixtures (Dieckelmann, *Ger.* 1,068,690). Purification by removal of sodium sulfate from alkylbenzene sulfonates was achieved with ethanol (Sullivan and Ptasinski, *U.S.* 2,952,639). Dissolution of impurities in ethylene dichloride resulted in purification of salts of detergent amino acids (Anderson, *U.S.* 2,993,071). The odor of

phosphine present in sulfoalkyl esters of fatty acids was substantially eliminated by hydrogen peroxide treatment (Scheneck, *U.S.* 2,999,871).

Separation of alkyl sulfates into detergent primary and wetting type secondary alcohol derivatives was accomplished using acetone as a solvent (Karnaukh and Deinekhovskaya, *U.S.S.R.* 133,879). Separation of polyethyleneglycol from nonionic surfactants for improved activity was accomplished using counter current distribution extraction with n-butanol-water (Nagase and Sakaguchi, *Kogyo Kagaku Zasshi* 64, 635-638). Anionic Sulfonates are recovered by precipitation with zinc amines (Erben, *Czech.* 89,046).

Depressed foaming and shortened reaction time was experienced when an aliphatic silicone was present during fatty

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H. BOOK REVIEW

alcohol sulfation (Oneto, *Brit. 852,968*). Sulfated fatty alcohols were formed using a N-lower alkyl ethylene carbamate-sulfur trioxide complex as sulfating agent (Smith and Harrington, *U. S. 2,957,014*). Pure surfactant sulfonates were prepared using chlorosulfonic acid as sulfonating agent (Lindner, *Ger. 1,070,623*). Unsaturated fatty alcohols were sulfonated with a mixture of chlorosulfonic acid and sodium hexametaphosphate (Schwarz et al., *Ger. 973,959*).

A Hungarian high pressure process was described for manufacturing fatty alcohol sulfates (Zilahi, *Man-Made Textiles*, 38, No. 443, 51-52). A process for continuous sulfonation of fatty alcohols with chlorosulfonic acid was patented (Weiss, *Ger. 1,078,116*). Oleic or elaidic acids were alpha-sulfonated using dioxane-SO₃ and their properties determined (Weil et al., *JAOCs 37*, 679-682).

Neutralization of strongly acidic constituents in fatty acylsulfonates was accomplished by adding soap (Unilever, Ltd. *Brit. 843,593*). A dry powdered product of organic sulfoxy acid was obtained by neutralizing in the presence of powdered solid carbon dioxide, the low temperature preventing hydrolysis and decomposition (Blinoff and Braude, *U. S. 2,975,141*).

Deaeration and purification of alkylbenzene sulfonate built detergents was effected by adding certain nonionic polyether surfactants to the slurry (Davis, *U. S. 2,952,638*). Mechanized production of detergent powders was described (Ranny, *Prumysl potraavin 12*, 308-312). A particulate detergent composition was achieved by spraying a detergent builder with an alkylaryl sulfonic acid, for example, dissolved in alkylene glycol, 1-4C atom alkanols and concentrated sulfuric acid (Dvorkovitz and Goldman, *U. S. 2,982,736*).

Ethylene oxide adducts of tall oil and other fatty acids were purified and improved by ozone treatment (Karabinos and Ballun, *U. S. 2,954,369*). Sodium tallow methyl taurate can be made fluid for pumping purposes, by adding specific quantities of a water soluble soap, maintaining a specified water content and temperature range (Kelley, *U. S. 2,962,447*).

Raw Materials

A five-fold increase in nonionic surfactant production since 1950 was noted (Berger, *Soap Chem. Specialties 37*, No. 3, 45-47, 106-107), and predictions for increased usage were made. The source and preparation of raw materials for nonionic surfactant manufacture were reviewed (Rao et al., *Chem. Age [India] 11*, 529-540). The added reactions of ethylene oxide to laurylamine and to lauric acid were described (Nagase and Sakaguchi, *Kogyo Kagaku Zasshi 64*, 1031-1034, 1035-1040).

Alkylaryl sulfonates were prepared from paraffin hydrocarbons of shale oil (Stepanova, *Izvest. Akad. Nauk, Eston, S.S.R. Ser. Fiz.-Mat. i Tekh. Nauk 10*, No. 1, 40-48), while five commercial tetrapropylenes of different origins were evaluated for the production of benzene sulfonates (van Embden, *Fette, Seifen, Anstrichmittel 63*, 456-460). Gas oils from two sources were converted into alkane sulfonates (Bathory and Lorincz, *Magyar Kem. Lapja 16*, 17-23).

Nekal type surfactants were prepared from filtered anthracene oil and from raw phenanthrene (Mazonski and Lachowicz, *Koks, Smota, Gaz. 3*, No. 3, 88-92).

Lamepons were prepared by Schotten, Baumann reaction of a fatty acid chloride and partly degraded albumin or casein protein (Sabeta, *Grasas y aceites 10*, 275-278). Ricinoleyl alcohol was shown as a satisfactory raw material for alkyl sulfate preparation (Achaya, *J. Chem. Eng. Data 6*, 38-42).

Fluorescent brighteners were reviewed (Adams, *Indian Oil & Soap J. 3*, 56-73), and used in an ethylene oxide-alkyl phenol surfactant composition (Auchincloss and Parker, *Brit. 833,201*).

Finely divided polyphosphate was made by dissolving their hydrates in glycerol or glycols, the colloidal form then being useful in built milled bars or flake soap or surfactant products (Blinka, *U. S. 2,940,938*).

The efficiency and other features of carboxymethyl cellulose (NaCMC) were discussed. Effectiveness depends upon nature of the surfactant, nature and concentration of other ingredients in the composition, and degree of washing (Pilpel, *Research [London] 14*, 319-325). The degree of polymerization of NaCMC was indicated as optimum between 200 and 500 and the degree of etherification only high enough for good water solubility (Smola and Skoda, *Fette, Seifen, Anstrichmittel 62*, 1123-1135). The ability of NaCMC to prevent subsequent soiling when applied in a final laundering rinse was claimed (Seegrist, *U. S. 2,979,373*). NaCMC is replaced in whole or in part with a polyvinyl ether of diethylene glycol to yield a more efficient redeposition preventing agent (Stillo et al., *U. S. 2,981,692*). Pairs of cellulose derivatives as soil redeposition preventives were claimed as more effective than

a single agent when used in detergent compositions (Reich and Dallenbach, *U. S. 2,994,665*). Sulfomethyl cellulose was claimed as an effective agent to prevent soil redeposition (Moech Domsjo Aktiebolag, *Brit. 846,217*).

Synthesis

NONIONICS. Ethylene oxide adducts with compounds containing 6 to 150 carbon atoms and a reactive hydrogen atom were reacted with P₂O₅ under substantially anhydrous conditions (Nunn and Hesse, *U. S. 3,004,056*). The reaction is also conducted in the presence of catalytic amounts of hypophosphorous or phosphorous acid or its salts (Nunn and Hesse, *U. S. 3,004,057*). Ethylene oxide adducts of sebacic acid residues were prepared (Niederhauser, *U. S. 2,969,388*). The reaction of ethylene oxide under pressure with various hydrophobes was studied (Nagase and Sakaguchi, *Kogyo Kagaku Zasshi 64*, 1043-1047).

The reaction velocity of ethylene oxide with various alcohols was determined (Ishii and Ozeki, *Kogyo Kagaku Zasshi 63*, 1387-1390). A demulsifier was obtained by reacting alkylene oxides with fatty alcohols (Levchenko et al., *U.S.S.R. 131,851*). Another demulsifier series was developed by reacting ethylene oxide with paraffin oxidation products (Nel'kenbaun and Mamina, *U.S.S.R. 132,754*). An emulsifier was obtained by reacting ethylene oxide with castor oil (Kirkpatrick et al., *U. S. 2,971,965*).

Pure polyethylene glycol stearates were prepared and their properties determined (Ito et al., *Takamine Kenkyusho Nempo 10*, 44-51). Effective wetting agents were produced by reacting ethylene and propylene oxides with branched chain alcohols (Chiddix et al., *Ger. 1,059,401*). Ethylene oxide adducts of branched chain alcohols were claimed (Esso Research and Eng. Co., *Brit. 857,434*). Another ethylenepropylene oxide type product was developed (Matsuda and Yonezu, *Japan 791* [61]).

Claimed were polyalkylene oxide adducts of polyfunctional organic acids (Heyden and Dieckelmann, *Ger. 973,985*). A polyoxyalkylene oxide adduct with a terminal hydrogen or alkyl group was formed (Bruson and O'Day, *U. S. 2,979,985*). A mixed polyalkylene glycol ether was produced by reacting polypropylene glycol and paraformaldehyde (Konishi and Hirao, *Japan 8949* [60]). Polyglycol ethers resulted from the reaction of oxyalkylating agents with a styrene derivative and a phenol (Farbenfabriken Bayer A.-G. *Brit. 854,952*). An emulsifier resulted from the reaction of oxyalkylating agents with cyclohexanol and fatty acids (Cardy et al., *Brit. 862,264*).

A class of nonionic surfactants is represented by the various polymer types. Glycidyl and glyceryl ethers of the block polymer type were synthesized and their properties determined (Kuwamura, *Kobunshi Kagaku 17*, 175-182).

Polyoxypropylene polymers were reacted with ethylene-propylene oxides to form surface active, low foaming agents (Wyandotte Chemicals Corp. *Brit. 855,010*). Solution polymerization of vinyl acetate with higher alcohols produced materials which, when saponified had surface activity (Sakurada et al., *Kobunshi Kagaku 17*, 120-125; Konishi and Ishizuka, *Ibid.*, 125-134; Konishi, *Ibid.*, 249-256).

Surfactant copolymers were obtained by reacting alkylmethacrylates with methacrylate esters and methacrylic acid (Stuart et al., *U. S. 2,993,032*). Esters of polymerized polyethenoid fatty acids were surface active (Kirkpatrick et al., *U. S. 2,987,490*). Polymeric ethers resulted from the polymerization of alkylene oxides such as styrene oxide, with a compound having a reactive hydrogen atom. These prepolymers are then reacted with ethylene oxide (Lundsted, *Ger. 1,086,438*). An aliphatic alcohol was treated with mixed ethylene-propylene oxides, then with ethylene oxide to effect water solubility (Steele et al., *Ger. 1,054,239*).

Epoxidized fatty acids were reacted with compounds like glycols, then treated with polyamines to produce surfactants (DeGroote and Cheng, *U. S. 2,956,067*). Lipophilic surfactants were produced by oxyethylating the reaction product of an aliphatic acid with a polyamine (Lewis, *U. S. 2,970,153*). Surfactants resulted from the reaction of propylene oxide and nitrogen-containing active hydrogen compounds (Lundsted, *U. S. 2,979,528*). Polymeric surfactants resulted from the reaction of multi-nitrogen molecules with several reactive hydrogen atoms and propylene oxide (Lundsted and Langdon, *Ger. 1,081,226*).

Another interesting class of nonionic surfactants is derived from mono- or poly-saccharides. Fatty acid monoesters of α -methyl-D-glucoside and their polyoxyethylene derivatives were effective surfactants (Komori et al., *Kogyo Kagaku Zasshi 64*, 177-183). Two types of polyoxyethylated glucosides were prepared and evaluated. Type A was derived by etherification of glucoside esters and Type B was obtained by esterification of methyl glucoside ethers (Otey et al., *JAOCs 38*, 517-

520). Fatty acid esters of diglucosylurea are good surfactants (Stevermark et al., *Ind. Eng. Chem.* 53, 212-214). Alkyl ether glucosides have high surface activity (Pollitzer, *U.S.* 2,974,134). The condensation product of a hydrophobic amine with a reducing sugar followed by oxyethylation produces effective wetting agents (Pollitzer, *U.S.* 2,976,275). The surface active characteristics of sucrose esters and glycerides were determined (Nobile, *Parfum. Cosmet. Savons* 4, 277-281). Described and evaluated were alkyl sucrose and ether-linked sucrose from glycidyl ethers (Gaertner, *JAOCs* 38, 410-418). Surfactants resulted from the reaction of aldose sugars, from the saccharification of wood, with methyl stearate (Udic Societe anon. *Brit.* 839,728).

Solid nonionic surfactants were produced by combination with urea. (Desty and Harbourn, *Ger.* 1,041,626). Amides were prepared by reacting lecithin with polymethylene diamine (Sincroft and Sipos, *U.S.* 2,987,527).

Products stable in solution were prepared of polyethylene glycol esters of 2-carboxyethylsilanes (Schmidt, *U.S.* 2,991,301). Polymer surfactants such as polyvinylated nonionics of the polyoxyethylene series were prepared and evaluated (Konishi and Ishizuka, *Yukagaku* 10, 11-18). The oxidation of ether- or ester-type nonionic surfactants was prevented by addition of hydroquinone or catechol (Nemoto, *Japan* 9829 ['60]).

AMPHOTERIC. A surfactant of this type was produced by reacting a hydroxyalkyl alkylene diamine with a fatty acid, then with sodium chloroacetate (Walker, *U.S.* 2,970,160). An alkyl glycidyl ether may be reacted with sodium methylaminoethane sulfonate to yield an amphoteric surfactant of the sulfonic acid type (Konishi et al., *Japan* 755 ['61]).

CATIONICS. Diquaternary ammonium softening agents were prepared by reacting tertiary amines and diamides (Matter et al., *U.S.* 2,984,587). Polypeptide type quaternary ammonium derivatives were prepared by using hydrolyzed gelatine, forming the chloroacetylated hydrolyzate and condensing with a tertiary fatty amine (Bolle et al., *Proc. Intern. Congr. Surface Activity*, 2nd, London, 1957, 4, 70-75).

ANIONICS. Alkylaryl sulfonates (Ben'kovskii et al., *U.S.S.R.* 136,502). Sulfonated alkylarene hydrocarbons C_{17} to 23 (Hale et al., *Brit.* 860,839). The sulfonation product of toluene reacted with pentenes was used to be a satisfactory detergent (Ashimov et al., *Azerbaijdzhan. Shim. Zhur.* 1960, No. 5, 65-72). The reaction product of alkylated aromatic hydrocarbons with alginic acid were useful oil emulsifiers (Linn, *Ger.* 1,053,488). Alkaline earth sulfonates of oil-soluble mahogany sulfonic acids (Blumer, *U.S.* 2,961,403). Wide thermally cracked gasolines can be used to produce alkylarene sulfonates and secondary alcohol sulfates (Anastasian and Jelaseo, *Chim. & ind.* [Paris] 85, 413-420).

Aliphatic or alicyclic monocarboxylic acids are reacted with an isethionate (Schenck, *U.S.* 3,004,049, and General Aniline & Film Corp. *Brit.* 835,519). Acylated hydroxy sulfonates were produced by reacting dehydrated fatty acids with an isethionate (van Alphen and deJong, *Brit.* 848,463). Similarly, fatty acids are reacted with an isethionate and p-toluene sulfonic acid (same patentees, *Brit.* 853,590). Details to prevent foaming in similar systems were disclosed (van Alphen and Terwan, *Brit.* 869,744).

Glyceryl sulfates are produced for detergent usage (Gray, *U.S.* 2,979,521, division of *U.S.* 2,868,812). A process through the epoxide to a glyceryl ether sulfonate was described (Whyte, *U.S.* 2,989,547).

A new series of monoalkyl sulfo succinates was described (Vallee, *Parfum. Cosmet. Savons*, 4, 205-207). Properties and synthesis of docosenyl sulfates were reported (Komori et al., *Yukagaku* 10, 153-159). Surfactants were produced by reacting higher molecular weight aldehydes with sodium bisulfite (Minamiyama and Nishimura, *Japan* 9025 ['60]).

Fatty acid-methyl tauride products were disclosed (Schwalenberg, *Ger.* 1,067,825). Urethans were prepared for example by reacting alkyl chloroformates with N-alkylamino carboxylic or sulfonic acids (Orthner et al., *Ger.* 1,097,431). Phenol aminosulfonate products were prepared and evaluated (Gaertner, *JAOCs* 38, 212-215). High molecular weight sulfonated alkanesulfonilides were described (Schwalenberg, *Ger.* [East] 19,650). Fatty acid esters of hydroxyalkane sulfonic acid amine salts were prepared (Sexton and Britton, *U.S.* 2,968,664). Alkylolaminohydroxy fatty products were patented (Findley and Robin, *U.S.* 2,993,919). Detergents of fatty acyl-aminomethane sulfonate composition were prepared (Alsbery et al., *Brit.* 830,054). Hydroxyalkylamide sulfates were described (Rabinovich and Skripchenko, *Novosti Pishch. Prom.* 1959, Nos. 3-4, 20-24). Derivatives of ampholytic surfactants were sulfonated to give anionically acting products (Mannheimer and McCabe, *Brit.* 853,440). Fatty alkylol amine products are reacted with chloroacetic acid and these sodium salts have surfactant properties (Mannheimer and McCabe, *Brit.* 853,441).

A series of surfactants were made by direct connection of the phosphorous atom to long aliphatic chains, and their properties were determined (Kawata et al., *Yukagaku* 10, 159-164). Epoxytriglycerides were phosphorylated in 85% phosphoric acid and a suitable solvent (Findley, *U.S.* 2,965,657). High mol wt aliphatic polysulfonium surfactants were prepared by reaction of high mol wt aliphatic polythio ethers with monofunctional alkylating agents (Enders and Holt-schmidt, *Ger.* 1,062,014). Emulsifiers or thickeners resulted by conversion of HCN polymers with ethylene oxide (Völker and Walter, *Ger.* 1,065,423).

Fluorocarbon surfactants were reviewed (Komori, *Yukagaku* 10, 2-5).

Mixtures of surfactants for improved characteristics seem to be appearing in greater volume. A mixture of alkylated aromatic mononuclear hydrocarbon sulfonates is treated with fatty alcohols for improved emulsifiability (Lindner, *Ger.* 973,482). A mixture of detergent sulfonic or sulfuric acids and an amphoteric surfactant is described (Mannheimer, *U.S.* 2,993,918). Mixed for improved properties were dodecylbenzene sulfonic acid and sulfonated oleic acid (Wylie et al., *U.S.* 2,995,524). Mixed for the same reason were alkyl sulfonic or sulfuric salts and fatty acid amides (Wilson, *U.S.* 2,965,576), sulfonation of dodecylbenzene and sperm alcohol mixtures (Noda et al., *Japan* 668 ['61]), amphoteric surfactants with nonionics (Masci and Poirier, *U.S.* 2,999,069), and an aliphatic monocarboxylic reaction product with a diamine, and this mixed with a nonionic (Masci and Poirier, *Ger.* 1,084,414).

An oil soluble dodecylbenzene sulfonate was converted from the water soluble equivalent by conversion with ammonia (Murai et al., *Japan* 8219 ['60]). Anionic or cationic surfactants were mixed with acyclic alkylmonoamines (Wilson, *Ger.* 1,034,307). Alkyl sulfonates or sulfates were mixed with potash soaps to form solid compositions (Sheely and Glynn, *U.S.* 2,991,253).

Compositions

ANTISEPTIC. Quaternary ammonium compounds with condensed phosphates and primary amines have been used (Wisensemeier and Kehrer, *Ger.* 1,107,364). Quaternary ammonium salts alone or with benzylphenols are added to molten fatty acid-alkali mixtures and cooled to form bars (Schraft, *Ger.* 1,091,265). Quaternary ammonium compounds were tested successfully for milk plant disinfection (Cousins et al., *J. Appl. Bacteriol.* 23, 359-371).

Fatty diethanolamides and phenolic sanitizers were useful as floor cleaners (Moculeski et al., *Soap Chem. Specialties*, 37, No. 4, 58-59). Soaps containing chlorinated phenols are not discolored when sodium thiosulfate and sodium polyamino polycarboxylates are added (Prosch, *Ger.* 1,094,908). Acid resistant surfactants were required for pastes or solutions of a variety of disinfectant agents (Rodger, *Ger.* 1,105,549). Stable germicidal solids were obtained by combining anionic or nonionic surfactants with a germicidal phenol and an acid material such as citric acid (Maurice and Payne, *Ger.* 1,074,189).

Anionic or nonionic detergents were rendered antiseptic by adding chlorosubstituted thiocarbonyl (Beaver and Stoffel, *Brit.* 846,922). For similar surfactants 3,5-dichlorosalicyl-3,4-dichloroanilide is preferred (Owen, *Ger.* 1,081,173). For a sodium dodecylbenzene sulfonate detergent 3,3',4',5-tetrachlorosalicyldichloroanilide was used (Colgate Palmolive Co. *Brit.* 848,306). A variety of tri- and tetrachloro benzanilides were used with anionic or nonionic surfactants (Beaver and Stoffel, *U.S.* 2,965,575).

Iodine, in a liquid mixture of phosphoric acid, surfactants, and urea was said to be a good germicide (Scheib et al., *U.S.* 2,977,315). A nonionic-iodine surfactant was patented (Shelanski and Fair, *U.S.* 2,931,777).

A milky emulsion of an amphoteric surfactant, an organic acid and a fatty monoethanolamide was recommended for surgical disinfection (Th. Goldschmidt A.-G., *Brit.* 836,956 and 848,654). A disinfectant stick was formed from alkyl sulfates, phenylmercuric oleate and lactic acid (Rödiger, *Ger.* 1,092,148). Amine complexes of zinc dimethyldithiocarbamate were used in bacteriostatic compositions (Taylor, *U.S.* 2,977,316). Soap compositions contained silver-form ion-exchange resins to kill bacteria (Lutz and Sharpe, *U.S.* 2,951,811).

BAR COMPOSITIONS. The manufacture of toilet soap was reviewed (Gattoni, *Grasas y aceites* 11, 270-277), while the necessary characteristics and properties of molded syndets were described (Manneck, *Parfum. Cosmet. Savons* 4, 282-288). Soap bars containing phenolic bactericides were stabilized by adding aliphatic monocarboxylic acid hydrazides (Harshman and Fusco, *U.S.* 2,963,438).

Claimed was a bar comprising the ammonium and alkali or alkali metal salt of n-alkyl sulfonates and water (Clippinger, *U.S.* 3,001,948). Closed die moldings were made of sodium

alkyl glyceryl ether sulfonates and other minor ingredients (Lundberg and Blinka, *U. S. 2,987,484*). The sulfates of mixed alcohols from coconut oil and tallow were used (Sinnova S. A., *Fr. 1,111,670*), while glucose added to the active ingredients gave lower cost (*Fr. addition 68,013*). A bar product was claimed comprising an anionic sulfate, soap, hydrated magnesium soap and an electrolyte (Chaffee, *Ger. 1,047,974*). Alkane sulfonates were claimed not to need organic binding agents (California Research Corp., *Brit. 861,052*). Alkyl glyceryl ether sulfonates, soap, and magnesium or calcium soaps or starch were used (Mills and Korpi, *Ger. 1,076,865*), and the same type product was covered (*U. S. 2,988,511*).

Fatty acid hydroxylamine sulfates and soap, with lanolin and polyethylene glycol were claimed for bar use (Hennig, *Ger. 1,108,368*). A paste of sodium alkylarylsulfonate and a sugar substance was extruded as a bar (Hug, *Ger. 1,081,993*). Sodium dodecylbenzene sulfonate was added to 30-45% glucose to give a solid (Sinnova S. A., *Fr. addn. 68,929 to Fr. 1,111,670*). A cake was formed of 1-(4-sulfophenyl)dodecane, alkylbenzene sulfonate and tallow alcohol (Hewitt, *U. S. 2,972,583*). Bars were formed from N-methyl-N-sorbitylauramide, urea, and dodecyl sulfate (Boettner and Rainey, *U. S. 2,982,737*). Fatty methane sulfonate products were combined with soap as ingredients for bar stock (Alsbury et al., *Ger. 1,074,977*).

Soap and the reaction product of phosphorous oxychloride with polyethylene glycol were used in bars (Nüsslein, *Ger. 973,122*), as were mixtures of soap and the reaction product of high mol wt hydroxy amines with phosphoric acid and phosphorus pentoxide (Schmitz, *Ger. 1,097,071*).

Soap combined with mono- or distearates form satisfactory bars (Praetorius and Hiller, *Ger. 1,079,772*). Improvement in the skin of soap bars containing fatty alkyl sulfates was claimed by adding a fatty hydroxyalkylamine (Weiss, *Ger. 1,051,442*). Disinfectant cakes were claimed for mixtures of soap with urea and an alkylamino carboxylic acid (Cramer and Schmitz, *Ger. 1,047,975*).

Toilet soap was prevented from darkening by adding sodium silicate (Zaliopo, *Masloboino-Zhirovaya Prom. 26, No. 10, 40-41*).

A protective coating for bars comprised, for example, a solution of polyacrylamide (Eohr and Rennar, *Ger. 1,089,907*).

Various types of wax were claimed as detergent bar builders (Blinka and Grounds, *U. S. 2,982,735*).

LIQUID LIGHT DUTY COMPOSITIONS. A brief review with some formulations was made (Reims, *Chem. Prods. 24, 365-366*). A concentrated liquid was produced comprising 30% C₁₂₋₁₆ alkylbenzene sulfonate, 5% sodium toluene sulfonate and 1-2% of a polyethylene glycol (Fein and Friedman, *U. S. 2,978,416*). Another composition comprised 10-50% alkylaryl sulfonate mixed with secondary alkyl sulfate and alkylphenyl polyoxyethylene glycol (Kooijam et al., *U. S. 3,000,832*). Various organic and inorganic bases were described as neutralizers for alkylbenzene sulfonic acids used in light duty liquids (Gluckman, *Soap Chem. Specialties 37, No. 7, 43-46, 99-100*). Clear solutions were obtained by adding certain polyoxyethylene esters or ethers to mixtures of alkylbenzene sulfonate and fatty alcohol sulfates (Pulcra Limitada, *Span. 249,896*). Viscosity of a nonionic sulfate and triethanolamine salts of alkylbenzene sulfonates is controlled by adding portions of magnesium alkylarene sulfonates (Duperray, *Fr. 1,233,047*). Liquid detergents were comprised particularly of magnesium compounds corresponding to normal dialkylarene sulfonates (Duferray, *Chim. & ind. [Paris] 84, 375-381*).

The sulfate of alkyl or aralkyl polyoxyethylene adducts is used in conjunction with normal builder additives and another anionic, such as alkylbenzene sulfonate to which hydrogen peroxide may or may not be added (Best, *Brit. 855,679; 855,893*). Cold-resistant liquids may be produced by the simultaneous sulfonation of an alkyl, aralkyl or alkylamine ethylene oxide adduct and an alkylphenol, then neutralizing with magnesium or ammonium hydroxide (Sinnova Sadie, *Fr. addn. 68,303 to Fr. 1,079,974*). A sulfated polyethoxyalkylphenol is neutralized with an excess of substituted aminoamide (Masci and Poirier, *U. S. 2,999,069*). An opaque liquid contained, for example, sodium (coconut) alkyl ethylene oxide ether sulfate, sodium (coconut) alkyl glyceryl sulfonate, sodium (tallow) alkyl glyceryl ether sulfonate, coconut fatty acid monoethanolamide and minor amounts of inorganic salts (Thos. Hedley & Co. Ltd., *Brit. 847,712*). Another opaque liquid was produced by mixing together an anionic syndet sodium salt, sodium C₁₆₋₁₈ alkyl glyceryl ether sulfonate, ethanol or propyl or isopropyl alcohol, and sodium toluene sulfonate (Walker and Blinka, *U. S. 2,970,963*).

Liquid or pasty detergents were claimed containing phosphoric acid esters of polyhydric (sugar) alcohols or nitrogen containing alcohols (Huttenlocher et al., *Ger. 1,062,380*).

A clear homogeneous liquid is claimed comprising an alkylamine oxide, an ethylenediaminetetraacetate or similar compound, and a benzene, toluene or xylene sulfonate (Drew and Zimmerer, *U. S. 3,001,945*).

SHAMPOOS. Preparation, formulation and mildness testing of lauryl sulfates were discussed (Anon, *Indian Oil and Soap J. 10, 364-366*). Claimed was an acyl C₁₂₋₁₈ isethionate mixed with an acylated C₁₂₋₁₅ polypeptide and a fatty acid ester of a polyhydrated alcohol (Powers and Barnett, *U. S. 2,972,582*). An opaque pearlescent liquid was comprised of a sodium or potassium alkyl glyceryl ether sulfonate, alkyl C₁₆₋₁₈ sulfonate and an amine oxide (Pileher and Eaton, *U. S. 2,999,068*). Claimed was a mixture of acyl C₈₋₁₈ monoglyceride monosulfate and a small amount of water soluble polyacrylamide to increase viscosity (Hansen, *U. S. 3,001,949*). A shampoo was prepared from a mixture of a cation-active compound free from imidazoline rings and containing at least one basic nitrogen atom and one aliphatic radical, with sufficient tert-dodecyl mercaptan polyoxyethylene thio ether (Albrecht and Matter, *U. S. 2,992,994*). Synthetic fatty acids from paraffin oxidation are sulfonated and neutralized with monoethanolamine for use in shampoo preparations (Sukhoter, *U.S.S.R. 131,435*). A detergent useful in shampoo formulations results from the reaction of an alkylaryl polyoxyethylene sulfate and the condensation product of sodium chloroacetate with a hydroxyethylaminoethylamine, and a further nonionic of broad character (Masci and Poirier, *Brit. 850,514*). The same general claim covers an alkylcarbonylaminopolyoxyethylene sulfate instead of the alkylaryl compound above, and N-(2-hydroxyethyl)-ethylene diamine instead of the previous -aminoethylamine (Masci and Poirier, *Brit. 820,515*). A shampoo is claimed of a quaternary ammonium surfactant, an alkanol such as glyceryl monostearate and either an ampholytic or nonionic surfactant (Schwartz, *Ger. 1,076,331*). A clear liquid was obtained by solubilizing sulfonated or sulfated surfactants with a mixture of fatty acid alkylolamide and a diol (Gillette Co., *Brit. 843,379*).

A germicidal shampoo comprises salts of surfactant betaines (Schmitz, *Ger. 1,062,392*).

Non eye-irritating shampoos were claimed comprising a cationic surfactant (0.4-7%), nonionic polyoxyalkylene surfactant (2-20%), and an imidazoline derivative (Gillette Co., *Brit. 847,570*).

The viscosity of a shampoo consisting of a soap and a sulfated or sulfonated anionic surfactant was controlled by adding 0.01-1% of a soluble aliphatic polyoxyalkylene compound (Wei, *U. S. 3,001,944*).

LIQUID HEAVY DUTY COMPOSITIONS. An opaque composition consists of dodecylbenzene sulfonate, potassium pyrophosphate, fatty acid monoethanolamide, ethanol, glycerol, propylene glycol and water (Pengilly, *U. S. 2,992,993*).

A concentrated liquid consisted of potassium alkylaryl sulfonate, an aryl or alkaryl hydrogroup sulfonate, potassium polyphosphate, fatty acid alkanolamide, and a pair of soil suspending cellulose ethers (Reich and Dallenbach, *Ger. 1,054,638 and U. S. 2,994,665*). Homogeneous suspensions comprised alkylbenzene sulfonates, potassium triphosphate and/or pyrophosphate, lower alkylbenzene sulfonates, coconut fatty acid diethanolamide, alkali cellulose glycolate, ethanol, and water (Harold and Wixon, *Ger. 1,051,440*). Homogeneous suspensions were prepared of potassium dodecylbenzene sulfonate, potassium pyrophosphate, sodium xylene sulfonate, lauric diethanol- and isopropanolamide, sodium silicate, cellulose derivatives and water (Unilever, Ltd., *Brit. 870,081 and Carroll, Ger. 1,038,695*).

An aqueous ammonium hydroxide composition contained by weight 1-26% ammonium hydroxide, at least 0.1% water dispersible anionic surfactant, water soluble dye, colloidal dispersed water-insoluble terpene compound, and a nonionic surfactant (A. and L. Stahler, *U. S. 3,001,947*).

Mixtures of alkyl diphenyl ether sulfonates and polyphosphates yielded stable liquids (Steinhauer and Valenta, *U. S. 2,990,375*). Heavy duty liquids composed of alkali metal glyceryl ether sulfonates, potassium pyro- or triphosphate, sodium silicate, alcohol or diethylene glycol monobutyl ether were described (Thos. Hedley & Co. Ltd., *Brit. 848,224*).

Concentrates were obtained using mixtures of alkanol polyoxyethylene adducts and high mol wt polyphosphates (Lindner, *Ger. 1,080,722*).

A liquid composition meant for dishwashing machines was comprised of sodium orthosilicate (4.5-6%), sodium metasilicate pentahydrate (2.5-3.5%), potassium triphosphate (5-7%), arene sulfonate (14-18%), water (60-80%), and a nonionic surfactant of low foaming capacity (4-6%) (Silberman, *U. S. 2,979,466*).

The compatibility and stability of solutions of soluble silicates and mixed phosphates for heavy duty liquid detergents

were described (Getty and Stricker, *Soap Chem. Specialties*, 37, No. 6, 45-47, 114, 116-118).

SOAP COMPOSITIONS. An anhydrous free-flowing quick dissolving powder results from a mixture of a finely divided two molar amount of fatty monocarboxylic acid intimately mixed with one mole of sodium carbonate (Curtin, *U. S. 2,992,992*). Molten soap with at least 50% acid unsaturated radicals and sodium carbonate are sprayed and to the powdered mix di-sodium or -potassium orthophosphate is added (Parke, *Ger. 1,079,774*). Urea is added to a soap-borax mixture (U. S. Borax & Chem Co., *Ger. 1,095,976*). Alkali metal soaps are kept in solution by the addition of selected N-hydroxyalkyl derivatives of urea, thiourea, and others (Praetorius et al., *Ger. 1,093,032*). Soaps are maintained in solution by adding sodium N-(tallow acid radical)-N-methyl taurine (Unilever Ltd., *Brit. 848,633*).

Soaps are stabilized by adding 0.05-2.5% of acylated or acetylated products of phosphorous acid or its derivatives (Blaser et al., *Ger. 1,072,346*).

The ratio of free fatty acid to the aluminum ratio of such soaps can be controlled to give a pure aluminum di-soap (Bull-off, *U. S. 2,993,064*). A process is described for producing fine-grained, multivalent metal soaps (Meyer, *Ger. 1,054,446*). The properties and uses of various metallic stearates were described (Reed, *Am. Perfumer Aromat. 76*, No. 3, 49-50). Compositions for blowing soap bubbles were patented (Aktiebolaget Alfred Ullmann & Co., *Ger. 1,049,352*).

HAND CLEANERS. Skin irritation is said to be reduced by adding at least 0.1% of N-lauroyl sarcosine or its salts to alkylbenzene sulfonates or alkyl phenylpolyoxyethylene ethers (Dvorkovitz et al., *U. S. 2,962,448*). Gluconic acid and other organic acids are cited as reducing skin irritation by detergents (Dvorkovitz et al., *U. S. 2,982,739*).

A hand paste comprising soap, mineral oil thickened with calcium soap and water is cited (Belen'kel, *U.S.S.R. 135,189*). Hand cleaning gels are prepared from an alkane and fatty C₁₂₋₁₆ amide of sarcosine (Schmolka, *U. S. 2,982,738*).

Partially oxidized Fischer-Tropsch paraffin is deodorized by treatment with acetic anhydride, then neutralized with potassium hydroxide to give a paste (Müller, *Ger. [East], 19,575*).

SUGAR DETERGENTS. Diglycosyl urea monoester was combined with urea and possibly other detergent builders (York, *U. S. 2,981,691*). A detergent composition of urea and a mono fatty acid ester of diglucose ureide was claimed (York and Osipow, *U. S. 2,991,691*). Heavy duty detergents were prepared from at least one surfactant, a monoester of sucrose, and builders (Hass et al., *U. S. 2,970,962*).

CONTROLLED FOAMERS. One obvious method for controlling foam in detergent compositions, is to add a defoaming agent either to the composition or to the bath. Polyoxyalkylated doubly unsaturated fatty acid products are recommended (Mayhew and Ottley, *U. S. 3,000,835*). A nonaqueous composition for foam control comprises an oil, a water-insoluble metal soap, alkyl secondary amines, and a polyoxyethylene fatty acid ester (Lam, *U. S. 2,926,971*). Antifoamants for detergent compositions not reducing detergent action contained saturated fatty acid soaps and a mixture of, for example, polyethylene glycol stearate and hydrogenated tallow alcohol ester of polyethylene glycol (Stayner, *Ger. 1,089,906*). Foam suppressant products were prepared from tall oil pitch (Steiner et al., *U. S. 2,931,780*). A nonionic surfactant antifoam agent was prepared by reacting 1,2-propylene glycol with glycerol, followed by ethylene oxide addition (Pruitt and Rogers, *U. S. 2,948,757*). Foams caused by anionic or cationic surfactants can be destroyed by adding ion exchange resins capable of absorbing the surface active ion (Wilson, *U. S. 2,993,867*).

Another method to control foam is to add the inhibitor to the composition, and diethylsulfosuccinate foam is controlled by combination with diethylene glycol fatty acid monoester (Lawler and Ballou, *U. S. 2,969,332*). Low foamability detergents were produced using mixtures of saturated fatty acid soaps, sulfate or sulfonate anionic surfactants, and a nonionic polyoxyethylene surfactant whose hydrophobe was either an alkyl or alkylphenyl group (Stayner, *Ger. 1,085,998*). Another foam-controlled composition comprised an alkylphenyl polyglycol ether chosen for its low foam height when combined with the usual builders (Mayhew and Jelinek, *Ger. 1,088,175*). Foam of a mixture of nonionic ethylene oxide adducts of nonyl alcohol and a C₁₂₋₁₆ fatty alcohol mixture was reduced by adding tallow fatty alcohol and magnesium acetate (Böhme Fettechemie G.m.b.H., *Brit. 833,082*). A nonionic surfactant mixture comprised an alkylphenyl-formaldehyde condensate and the benzyl ether of alkyl phenoxy-polyethoxyethanols (Niederhauser and Lane, *Ger. 1,061,471*). Low sudsing nonionic and soap-synthetic mixtures were discussed (Tschakert, *Soap Perfumery & Cosmetics 2*, 179-198).

CORROSION INHIBITORS. The corrosion rate of soft steel, zinc, aluminum, and tin was determined in the presence of ten anionic surfactants and triethanolamine in aqueous solutions. Zinc was corroded by every agent tested and tin only by two (Kato and Sato, *Kogyo Kagaku Zasshi 63*, 1726-1729). The effect on the above metals by four ampholytic surfactants was determined (Kato and Sato, *Ibid.*, 1739-1942). An imidazole derivative was patented for light duty detergent usage to prevent corrosion of copper base alloys (Harris, *U. S. 2,992,832*). The discoloring action of polyphosphates on copper base alloy was controlled by adding dicyandiamide (Light, *U. S. 2,967,832*). Benzotriazolol was successful in inhibiting copper base alloy corrosion in light duty detergents (Heininger, *U. S. 2,969,329*). Triazoles and tetrazoles with acidic :NH or :NOH groups inhibited corrosion of phosphate and perborate containing surfactant solutions (Tanner, *Ger. 1,059,601*).

A polyoxyalkylene nonionic is chosen which will react with gluconic acid to control pH and inhibit corrosion of tin-plate (Hiyama and Tomiyama, *Japan 12,919('60)*).

Oxalate addition was claimed to reduce corrosion (van den Bosch, *Ger. 1,070,327*). A stannous compound added to a surfactant containing a peroxy compound controlled corrosion (Wolhoff, *Ger. 1,062,866*). The same stannous compounds and peroxy containing detergents were spray dried (Wolhoff, *Ger. 1,092,147*). Corrosion preventing compositions contained citrates, perborates, and polyphosphates (van den Bosch, *Ger. 1,078,724*).

A polyamine was used to prevent corrosion in a nonionic automatic dishwashing composition (McCune, *Ger. 1,081,590*; *U. S. 2,993,861*). Phosphated alkyl glyceryl ethers inhibited corrosion of aluminum, zinc, and copper base alloys by built detergents (McCune, *Ger. 1,079,773*). Corrosion by a built nonionic detergent was inhibited by using water-soluble silicofluoride (Tuvell, *U. S. 3,000,831*).

FOAM IMPROVED COMPOSITIONS. Sulfonated fatty acid alkylamine products are said to improve foam of built anionic surfactants (Weiss, *Ger. 1,092,592*). Built surfactants of all types were said to be improved by adding an amino-carboxylic acid amide (Kirstahler and Goldann, *U. S. 2,989,484*). A foam stabilizer for built anionic detergents is C₁₂H₂₅NH(CH₂)₃NHCOCH₂OCH₂COONa (Götte et al., *Ger. 1,102,956*). Dishwashing anionic detergents were improved by adding an alkylureaglycoside (St. John, *U. S. 2,985,592*). Built anionic detergents are foam-improved by adding high mol wt aliphatic amines condensed with sulfones (Götte and Gündel, *Ger. 1,071,873*). Ethylene oxide derivatives of fatty acid isopropanolamides are described (Scherr, *U. S. 2,991,296*). Lathering properties of anionic detergents are improved by adding dialkyl or alkylaryl sulfoxides (Unilever Ltd. *Brit. 846,636*; *U. S. 2,787,595*). An anionic built detergent was improved by the addition of an ethylene oxide treated benzene sulfonamide (Jelinek and Mayhew, *Ger. 1,061,470*). Low mol wt p-acylphenyl glycol ethers improved foamability of built anionic detergents (Spence et al., *Ger. 1,081,588*). Mixtures of octylphenyl polyoxyethylene ether and similar oleyl and cetyl ethers with alkylbenzene sulfonates had improved foam stability and solution clarity (Shepherd and Hill, *Brit. 870,458*).

Aluminum ion added to alkylaryl sulfonates, cellulose glycolate, pyrophosphate, and sodium sulfate gave better detergency than magnesium or calcium ion (Purger and Heidelmann, *Ger. 1,065,124*).

DRY CLEANING. Syndets are said to be replacing soap in chlorinated solvents. Important to a dry cleaning detergent is ability to solubilize water and disperse solvent-insoluble dirt within the solubilized water (Davidsohn, *Am. Perfumer Aromat. 76*, No. 3, 59-61). Water solubilization is increased by adding to the solvent, an alkali metal salt of a sulfonated dialkyl diphenyl oxide (Smith et al., *U. S. 2,992,999*). Improved detergency and redeposition prevention were said to be obtained by adding specific cationic, nonionic, and anionic constituents to the bath (Miller, *U. S. 2,980,624*). Solvent cleaning action was said to be improved by adding esters of higher fatty acids with mono- or disaccharides (Wedell and Goldann, *Ger. 1,080,719*). Cleaning activators exemplified by magnesium nonylphenoxyacetate were claimed (Gutmann and Heiss, *Ger. 1,084,865*).

Guanidine soaps of unsaturated fatty acids were claimed as dry cleaning detergents (Chamberlain, *U. S. 2,978,415*). Soil redeposition was prevented by adding high mol wt amines to conventional surfactants (Wedell, *Ger. 1,057,275*).

Dispersion stability was increased by adding a high mol wt thiuronium salt to the bath (Wedell and Dohr, *Ger. 1,054,634*). N-Hexadecylpyridine chloride is added to an organic solvent in textile cleaning (Garovoi, *U.S.S.R. 132,609*). The feel of dry cleaned garments was improved by adding polymers or copolymers of p-tert-butylstyrene (Friedrich et al.,

Ger. 1,088,019). Water-soluble stains were removed by using a mixture of oil or sulfonated oil, a weak acid, a weak alkali, and an aqueous soap solution (Bittenfeld, *U. S. 2,980,621*).

DISH AND GLASS DETERGENTS. Sodium lignosulfonate used with sodium hexahydroxyheptanoate successfully reduces corrosion of mild steel in bottle washing machine (Otrhalek, *U. S. 2,976,248*). A composition for glass and ceramic cleansing comprises a mixture of one or more surfactants mixed with an alkali metal palmitate, an alkylarene sulfonate film former, polyvinyl alcohol, water and urea (Becher, *Ger. 1,075,778*). Hard water scale is inhibited by adding a fructoheptonate to the usual bottle washing baths (Karabinos and Quinn, *U. S. 2,992,998*).

A photometer was developed to measure the entire glass surface to evaluate dishwashing compositions (Kimmel et al., *Soap Chem. Specialties 37*, No. 4, 51-54, 101, 103-104). A dishwashing rinsing composition was composed of an alkylbenzene sulfonate, a nonionic ethylene oxide surfactant, and soda soap in ethanol and water (Götte, *Ger. 1,088,173*). A rinsing agent contained alkyl sulfates or sulfonates, alkyl polyglycol ethers, alkali metal palmitates, polyvinyl alcohol, and an antibiotic such as aureomycin (Becher, *Ger. 1,095,435*).

Built dishwashing compositions contained an alkyl sulfate or alkylbenzene sulfonate, fatty monoglyceride monosulfate, and an alkyl urea glucoside to increase lather (St. John, *U. S. 2,985,592*). A glassware cleaner was comprised of the reaction product of a long chain amine, sodium 2-bromoethane sulfonate, and an acid chloride (Persico, *Ital. 568,675*). Porcelain surfaces are protected from calcium carbonate deposition by using isohypophosphoric acid salts in solutions used on the surfaces (Henkel & Cie. G.m.b.H. *Brit. 861,859*).

LAUNDRY AND TEXTILE COMPOSITIONS. Acetic or formic acid and a water-soluble ethylene oxide wax are added to a detergent suitable for synthetic fibers (Leidholt, *Ger. [East] 16,501*, addn. to *Ger. [East] 14,296*). Perfumes substantive to cotton or linen are added to detergents (Ritchie and Urwin, *Brit. 838,240*). A detergent containing active oxygen is improved for textile usage by adding either a carboxylic acid amide or its low mol wt polymer (Dithmar, *Ger. 1,093,773*). Deposits on textiles after washing are prevented by a rinse to bind multivalent metal ions. For this purpose, polyphosphates and ammonium salts of aminocarboxylic acids are used (Schmidt et al., *Ger. 1,102,329*).

Detergent mixtures effective in high electrolyte concentrations consist of dodecylbenzene sulfonate, and unsaturated monocarboxylic sulfonated oleic acid (Wylie et al., *U. S. 2,995,524*).

Detergent-softener compositions contain nonionic surfactants, builders, and hydrazinium compounds (Germann, *U. S. 2,995,523*). A scorch-resistant softening composition is composed of mono-, di- or triglycerides, a water-soluble high mol wt soap, a soluble heat labile ammonium or amine soap so that the pH becomes 9 or lower when the finish is heated (Lanner and Olney, *U. S. 2,978,408*).

Antistatic surfactants were compared on vinylon, acetate, and nylon by measuring surface electrical resistance. Many agents were tested and the results given (Takahashi and Nishikawa, *Yukagaku 6*, 148-152). Synergistic antistatic effects were not obtained by having nonionic and ionic radicals in the same molecule (Takahashi et al., *Yukagaku 10*, 168-174). Antistatic qualities result from mixtures of cationic agent with a large amount of inorganic salt and an anionic surfactant (Brunt and Williams, *Brit. 839,407*).

A washing and stiffening action can be achieved using swelling agents, such as cellulose ethers and other cellulose derivatives, alginic acid, or proteins in combination with poly- or pyrophosphates (Rieffert, *Ger. 1,029,113*).

Protein and albumin stains are removable from textiles in laundering by compositions containing a wetting agent, an emulsifying agent, and an alkali (Equipment commercial et industriel S.A. *Fr. 1,193,158*).

Polyamide fibers are washed with a mixture of nonionic surfactant and a compound of the formula $N[(CH_2)_nOO-(CH_2)_m]$ (Heinrich, *Ger. [East] 19,146*). Textile cleaners for use in high electrolyte concentrations are high mol wt aminosulfonic acids, exemplified by N-decyl-N-(2-hydroxyethyl)aminoethane sulfonic acid (Götte and Willmund, *Ger. 1,105,378*).

OXYGEN CONTAINING DETERGENTS. Many of the oxygen-containing detergents depend upon per-oxy compounds for their effectiveness. One spray-dried built detergent utilizes sodium perborosulfate as the source of oxygen (Hyatt, *U. S. 2,955,086*). Spray-dried detergent mixtures containing viscosity increasing agents utilize sodium perborate as the oxygen donor (Burger, *Ger. 1,071,874*). Soaps and anionic surfactants are mixed with oxidizing agents, then granulated (Grimm, *Ger. 1,051,441*). An alkylarenesulfonate includes sodium perborate and a soluble inorganic copper salt as cata-

lyst for the perborate, all as a dry mix (Kauffmann et al., *U. S. 2,975,139*). Calcium or magnesium salts are added to detergent compositions containing a per oxygen compound (Stüpel and Siegrist, *Swiss 341,936*). Per compounds are stabilized in detergent compositions by the addition of diethylenetriamine pentaacetic acid and magnesium silicate (Aiken and Howard, *Brit. 866,492*). Voluminous granular condensed phosphate perhydrates for detergent usage are prepared by blending sodium pyrophosphate or tripolyphosphate with hydrogen peroxide spray using magnesium silicate as a stabilizer (Chem. Fab. Joh. A. Benckiser G.M.B.H. *Brit. 861,381*). A built anionic detergent containing perborate also contains an activator obtained by reacting an acylating agent and phosphoric esters (Dithmar and Naujoks, *Ger. 1,107,632*). A built anionic detergent contains sodium perphosphate (Lindner, *Ger. 1,107,381*).

Another general procedure to arrive at available oxygen is to utilize compounds containing chlorine which can react to form hypochlorites. Effective agents for this purpose are isocyanuric chlorides and their salts, which were reviewed and their properties indicated as components of detergent mixtures (Lindner, *Fette, Seifen, Anstrichmittel 63*, 451-455). A built detergent composition containing di- or trichlorocyanuric acid was stabilized against decomposition by an olefin having a C:C bond, one of the carbons being tertiary (Colgate Palmolive Co. *Brit. 848,397*). As an addition to this patent the compositions were based on mixtures of abrasives (Colgate Palmolive Co. *Brit. 848,398*). Detailed were detergents containing an organic N-chloro compound (many are listed) which react with water at 40-80 C, and a surfactant compatible with the available chlorine donor (Wilson, *Ger. 1,074,188*).

Trichlorocyanuric acid compositions can be stabilized to moisture by addition of special heterocyclic compounds (for example, cyanuric acid) and these are effective in builder mixtures (Symes, *U. S. 2,980,622*). Built detergent compositions were claimed containing as an active chlorine donor the reaction product of NaOCl and disodium monoamidophosphate (Habernickel and Köster, *U. S. 2,980,506*).

In another spray-dried detergent composition useful for milk handling equipment, the available chlorine compound is dichlorodimethylhydantoin (Unilever, Ltd. *Brit. 869,085*).

Detergent bleaching compositions containing trichlorocyanuric acid are dedusted by adding silicones which do not adversely affect the stability of the chlorine donor (Harris et al., *U. S. 2,988,510*).

METAL CLEANER AND PAINT REMOVERS. Need for surfactants disposable in sewage disposal plants was mentioned, as was the growth of industrial usage (Speel, *Soap Chem. Specialties 36*, No. 9, 59-61, 115). Cleaning and polishing of kitchen ranges can be accomplished by using a mixture of nonionic surfactant, abrasives, and water soluble weak acids such as, phosphoric acid (Jodl, *Ger. 1,051,437*). A composition for rust removal comprised a soap emulsified in phosphoric acid, combined with a tertiary amine or N-substituted fatty amide (Collins et al., *Ger. 1,082,475*). A homogeneous solid high caustic cleaner was comprised of a surfactant and a sequestrant such as, NaOH-water (Brooker, *U. S. 2,987,483*). As a cleaner and rust remover, a silica gel was combined with an alkali metal nitrate or sulfate to control adhesives, a strong acid, a reducing substance, a surfactant, and solvent for fats and oils (Tilhaud, *Fr. 1,200,016*). A metal cleaning composition was composed of alkalis or alkaline salts and, for example, triethanolamine alkylpolyglycol thio ether sulfurate (Kallenbach and Bedbur, *Ger. 1,074,357*). Leaded and carbonaceous deposits can be removed from engines in three stages, first, in o-dichlorobenzene and water, then, a mixture of cresylic acid, alkali metal oleate and an alkali alkylarene sulfonate in water, finally a bath of o-dichlorobenzene and water (Bland, *U. S. 2,964,237*).

A composition suitable for cleaning and phosphating metal articles consisted of a chlorinated hydrocarbon containing 1-10% of at least one sorbitan monoester of an aliphatic acid having 1-6 moles of phosphoric acid per mole of sorbitan monoester (Sharp, *U. S. 2,986,482*).

A lime soap preventive was synthesized comprising the condensation product of ethylene oxide with a polymer of propylene oxide and a N base (Langdon, *U. S. 2,983,684*).

Paint removing compositions can be prepared by mixing a polyalcohol, olein, potassium hydroxide, butyl polyglycol, oleic acid-ethylene oxide adducts, water, turpentine oil, and dichloroethylene (Adam et al., *Ger. 1,088,174*). Cleaning of automobile painted surfaces without loss of gloss can be attained with an emulsion of dodecyl alcohol ethylene oxide adduct, paraffin, and aqueous ethanol (Wedell and Kirstahler, *Ger. 1,093,114*).

The free water content and form of tripolyphosphate control the characteristics of the detergent slurry formed. Preferred

compositions are given (Martin, *Ger. 1,054,636* and *1,054,637*).

MISCELLANEOUS. Finely divided detergents were produced directly by spraying an acid surfactant onto particulate builders (Dvorkovitz and Goldman, *U. S. 2,982,763*; *Ger. 1,068,848*). Low apparent density compositions were prepared by incorporation of compounds which react to form an inert gas during drying (Habicht et al., *Ger. 1,091,263*). Light density products were made by adding aluminum sulfate and sodium tripolyphosphate and soda ash to a surfactant (Industries chimiques de Voreppe, *Fr. 1,236,610*). Powdered products resulted from spraying liquid or pasty nonionic surfactants upon alkali metal phosphates (Pfrengle and Pietruck, *Ger. 1,098,132*). Nonseparating compositions were attained by controlling the density and size of spherical particles within given limits (Lindner, *Ger. 1,058,675*). Nonagglomerating products were made by spray-drying an aqueous suspension of nonionic surfactant and soap with builders (Ruff, *Dutch 95,296*). Nonagglomerating mixtures in hot water were obtained by spray drying soap with xylenesulfonate and sodium carbonate (Reich and Kelly, *U. S. 2,940,935*). A granular product is obtained by spraying an acid mixture of surfactant and toluene sulfonic acid onto a mixture of sodium carbonate and tripolyphosphate in a rotating drum (Pengilly, *Ger. 1,106,018*).

A paperlike detergent was obtained by spreading an alcohol solution of soap or soap-syndet on films of alginate, gelatin, etc. (Wakabayashi and Yazawa, *Japan 13,933* [1960]).

A gel form composition was obtained by combining with a fatty amide of sarcosine an alkane in sufficient amount (Schmolka, *U. S. 2,982,788*).

Greasy coatings from kitchen walls and the like were removed by saponification in the paste of a mixture of carboxymethyl cellulose and an alkali (Bosch, *Spanish 25,082*).

A foaming composition resulting from storage under pressure, comprised an anionic surfactant, an aliphatic alcohol, a polyhalogenated hydrocarbon, and water (Folonari, *Ger. 1,066,310*). Polished objects are degreased in a solution of a polyoxyethylene ether in alcohol (Plating-Chemie N. V. *Dutch 96,993*).

A detergent resulted from boiling *chondrum ocellatus* with sodium hypochlorite, decolorizing with oxalic acid then combining with a polyoxyethylene ether (Furuya, *Japan 11,514* [1960]).

Radioactive contamination was removed by washing with a composition comprising EDTA, citric acid, alkyl sulfate and adjusting the pH to 3.5 with sodium hydroxide (Stevenson, *Brit. 856,377*, addn. to *763,547*).

Compositions whose solutions are buffered at definite pH values dependent upon temperature are outlined (Teichmann and Ueberschär, *Ger. [East] 17,936*). Another pH controlled composition contains ortho- or polyphosphates, magnesium oxide, and a nonionic or anionic surfactant (Hellsten, *U. S. 2,992,186*).

Self-acting detergents were prepared by combining enzymes with sodium sulfate, neutral or acid pyrophosphate or albumins (Leidholt, *Ger. [East] 14,296*).

A stain removing composition comprises a silica aerogel, a stain solvent and a liquid chlorinated hydrocarbon (Collins, *Brit. 831,792*).

ANALYSIS

General methods for determination of surfactants were reviewed (Walker, *Seifen-Ole-Fette-Wachse 86*, 595-596), while the detection, isolation and identification of surfactants were discussed (Rosen, *J. Soc. Cosmetic Chemists 12*, 98-106).

A colorimetric method was developed for the determination of small amounts of unsaponified fats in soap (Wilczynska, *Chem. Anal. [Warsaw] 5*, 663-669). Free and combined oleic acid in soaps were determined by a rapid volumetric procedure (Antonacci, *Chim. e. ind. [Milan] 42*, 375-377). Nickel soaps in spent fat hydrogenation catalyst were determined quantitatively by chromatography (Golendeev and Frolova, *Trudy Gor'kovsk. Politekh. Inst. 15*, No. 5, 28-30). Peroxides in fish oil soap were determined (Takei et al., *Yukagaku 6*, 166-168).

Gas-liquid chromatography was used for the analysis of linear detergent alkylates (Blakeway and Thomas, *J. Chromatography, 6*, 74-79). Paper chromatography may be used in the analysis of surfactants in general, the spraying reagents for the different surfactant types being noted (Tajiri, *Kogyo Kagaku Zasshi 64*, 1024-1027). Swelling agents in detergent mixtures can be identified by paper chromatography (Pfrengle and Hintz, *Fette, Seifen, Anstrichmittel 63*, 630-632).

The crystal stability of various soaps was noted during X-ray diffraction studies (Ogino, *Kogyo Kagaku Zasshi 64*, 1021-1024). Infrared spectra of several soaps were compared in α -, β -, γ -forms of the sodium salts (Kewano, *Nippon Kagaku Zasshi 81*, 1805-1808). Near infrared absorption spectroscopy

was used to differentiate between 1- and 2-mono-glycerides (Susi et al., *38*, 199-201).

The quantitative estimation of polyalkylene oxides and their derivatives, applicable to their analyses in admixture with anionic surfactants depends upon the polyalkylene oxide precipitation by the tetraphenyl boron ion, and titration of the precipitate with mercuric nitrate (Seher, *Fette, Seifen, Anstrichmittel 63*, 617-622). Analysis for nonionic surfactants in solution was dependent upon surface tension measurement (Levchenko et al., *Zavodskaya Lab. 27*, 408-409). Span nonionic surfactants can be determined by saponification to release the sorbitol moiety which is then periodate oxidized to formic acid, then coupled with chromotropic acid, and measured at 570 m μ (Gatewood and Graham, *J. Am. Pharm. Assoc., Sci. Ed. 49*, 678-680). Determination of polyoxyethylene glycols in selected cationic ethylene oxide products was made by treatment with ion-exchange resins supplemented by spectrophotometric and a dichromate total oxidation procedure (Kilheffer and Jungermann, *Anal. Chem. 32*, 1178-1180). Polyethylene glycol in nonionic surfactants was determined by ascending paper chromatography (Ginn et al., *Anal. Chem. 33*, 143-145).

Mixtures of ionic and nonionic surfactants were analyzed by separation and recovery of the components by batch ion exchange (Rosen, *JAOCs 38*, 218-220).

Difference between total sulfuric acid by acid hydrolysis and the sulfuric remaining after fatty compound extraction provided the degree of sulfation of sulfated oils (Liteanu and Elöpatoki, *Studia Univ. Babeş-Bolyai. Ser. 1*, No. 2, 137-144).

Ionic surfactants may be determined by the technique of high-frequency titration (Sakakibara and Komori, *Yukagaku 6*, 282-284). Sulfur-containing anionic surfactants can be identified by reacting triphenyltetrazoliumchloride with the surfactant and extracting the product with dibromoethane. A reducing agent such as sodium dithionite caused red color formation. Interfering substances were noted (Renault and Bigot, *Compt. rend. 25*, 1515-1516). The p-toluidine chloride procedure was accelerated by saturating the solution with sodium chloride (Paramonov, *Tekstil. Prom. 20*, No. 8, 41-43). Ionic surfactants may be reacted with neutral red to provide the two-phase titration procedure (Aoki and Iwayama, *Yukagaku Zasshi 80*, 1745-1749). Close correlation between the two-phase bromophenol blue and phosphotungstate methods was noted (Chung and Chou, *Hua Hsueh Shih Chieh 13*, 128-130). Toluene and xylene sulfonates remain in the aqueous layer of the two-phase bromothymol blue method, after determination of higher mol wt anionics, and are determined by ultraviolet spectroscopy (Heinerth et al., *Fette, Seifen, Anstrichmittel 62*, 825-826).

Germeicidal agents such as cresols may be determined in soap by precipitating the calcium salt of fatty acid, and the cresol in the filtrate is titrated against sodium hydroxide, the variation in surface tension serving as the indicator (Angelescu and Davidescu, *Rev. chim. [Bucharest] 9*, 511-515). A broad variety of commonly used soap germeicides can be determined by extraction with dimethylformamide, treatment of the residue with acidie, then basic alcohol. The ultraviolet patterns are typical of the various germeicides, and used to identify them (Jungermann and Beck, *JAOCs 38*, 513-515).

The inorganic constituents in detergent compositions are important parts of the mixtures. Inorganic sulfate can be determined by a complexometric technique (van Kamp and van den Hondel, *Anal. Chim. Acta 24*, 219-223). Methods were given for determination of silicates, phosphates, and sulfates in such compositions (Heinerth, *Fette, Seifen, Anstrichmittel 63*, 181-183). Phosphorus and boron were determined sequentially as the oxides in detergent powders by ashing followed by titration and precipitation techniques (*Analyst 85*, 922-923).

PHYSICAL CHARACTERISTICS

MICELLAR PROPERTIES. The micellar properties of acid soaps in aqueous systems were described (Spring, *Univ. Microfilms, L.C. Card No. MIC 60-4427*, 144 pps.). Measurement of pH was used to determine critical micelle concentration (cmc) and compared with specific conductance results (Lawrence and McDonald, *Proc. Intern. Congr. Surface Activity*, 2nd, London, 1, 385-387). The cmc of ternary combinations of hexadecyltrimethyl ammonium bromide, heptanol, and water was measured and discussed (Lawrence and Stevenson, *Ibid.*, 1, 388-394). Micelle formation in bile-salt solutions and quantitative solubilization of a number of liquids were discussed (Elkwall et al., *Ibid.*, 1, 375-383). The thermodynamics of micellar solutions of sodium lauryl sulfate were studied. The nonelectric part of the free energy of micellization is nearly independent of micelle size and is slightly greater than kT/C atom in the chain. The results of previous

investigators were confirmed (Stigter and Overbeek, *Ibid.*, 1, 311-318).

The cmc values for several anionic surfactants agreed with the pinacyanole titration and solubilization techniques (Demchenko, *Masloboino-Zhivovaya Prom.* 26, No. 9, 26-28).

Complex associations of molecules was given as the reason for four changes in toluene-soap solvation concentration curves, the first change conforming to conventional cmc (Demchenko and Dumanskii, *Doklady Akad. Nauk S.S.S.R.* 131, No. 1, 120-121). The electrostatic free energy of micelle formation was determined. The acid dissociation constant was related to this free energy. (Veis and Hoerr, *J. Colloid Sci.*, 15, 427-436.) The presence of micelles of oil-soluble soaps facilitated the dissociation of the soaps to produce stable micellar ions and to impart a stabilizing charge to polar particles suspended in such media. Solubilization of polar molecules in oil-soluble soap micelles involved coordination and sometimes hydrogen bonding (Baseom et al., *U. S. Dept. Com. Office Tech. Serv.*, PB Report 161,067). Micelle size and concentration dependencies were studied by light scattering. An existing equation was modified into a more exact form (Anacker and Westwell, *Proc. Montana Acad. Sci.* 19, 4-7).

Differences in anionic surfactant adsorption on cotton substrate were demonstrated as due to strongly retentive natural wax. High adsorption values occur with cotton retaining the waxy coating. Completely dewaxed cotton shows a minimum of adsorption without maxima at cmc. These data explain differences in reported adsorption results. Data with other surfactants are given (Ginn et al., *JAOCs* 38, 138-143).

SOLUBILIZATION. An equation was developed for the solubilization of aliphatic hydrocarbons in the hydrosols of potassium soaps from saturated fatty acids (Demchenko, *Ukrain. Khim. Zhur.* 27, 206-208). For similar soaps at 60C, it was shown that the solubilization equilibrium (L) was $L = k(n-7)^2$ where k was a coefficient characteristic of the solubilization, n the number of carbon atoms in the soap chain, and where no solubilization occurred with hydrocarbons ≤ 7 carbons in the chain (Demchenko, *Kolloid Zhur.* 23, 36-39). Temperature dependence of micellar solubilization in the 140-180C range of a variety of surfactant types using a dye solubilization technique showed the log of solubilization in both built and unbuilt solution directly proportional to temperature (Mankowich, *JAOCs* 37, 587-589). The effect of lower aliphatic alcohols on turbidity and foam of sodium oleate solutions was determined. Turbidity increased to a maximum then decreased, while foaming and foam stability decreased with increasing concentration and mol wt of the alcohol (Yurzenko and Storzh, *Nauk. Zapiski, L'viv Derzhav. Univ. im. Ivana Franka, Khim. Zbirnik* 46, No. 5, 48-52). Solubilization of radiotagged triolein in surfactant solutions was at a maximum with 10 molar ethylene oxide adducts. Nonionics showed high solubilization of triolein, whereas anionics did not. The findings suggested for these nonionic surfactants, that solubilization is an important, and possibly a controlling factor, in the mechanism of fatty soil removal (Ginn et al., *JAOCs* 38, 361-367). Mixtures of secondary alkyl sulfates and alkane sulfonates solubilized a mixture of trichloroethylene and fatty diamines, and these compositions were used to clean fatty and oily soiled textiles (Skripchenko et al., *Masloboino-Zhivovaya Prom.* 26, No. 12, 27-29).

The water solubilization capacity of dry cleaning detergents was determined, using the change in electrical resistance of selenium (Sato et al., *Yukagaku* 6, 104-107). A mixture of quaternary ammonium salts with improved solubility for water in dry cleaning usage was described (Nanba, *Japan* 1374 [60]).

BIOLOGICAL EFFECT. An infrared method was described for the biologically "soft" or straight-chain and "hard" or branched chain alkylbenzene sulfonates. The surfactants in detergents or sewage are hydrolyzed and extracted with light petroleum to remove fatty materials, then converted to the heptylammonium salt and selectively extracted from ethanol-water with petroleum ether (Ogden et al., *Analyst* 86, 22-29). Alkylbenzene sulfonates of C_{11-13} alkyl side chains with various degrees of branching were studied for ease of decomposition under reproducible biological filter conditions and in static river water. Ease of metabolism of branched chains increases as the chain becomes less branched and shorter (Burnop and Bunker, *Centre belge étude et document. eaux, Bull. trimestr. cebedeau* 4, No. 50, 262-268). Resistance to bacterial decomposition was associated with tertiary alkyl groups in the detergent molecule where a carbon atom is attached to three methyl groups. Large scale tests were carried out (Roberts, *Inst. Sewage Purif., J. Proc.* 1960, 469-472).

GENERAL PROPERTIES. The electron microscopy of surfactants and surfactant solutions in dilute and concentrated form was reviewed (Rösch, *Fette, Seifen, Anstrichmittel* 62,

661-668). Electron micrographs of sodium laurate samples were presented, showing that structure depends on initial solution concentration and method of drying (Rösch, *Ibid.*, 62, 811-817). Electron micrographs of sodium dodecyl sulfate and sodium alkylbenzene sulfonate were presented and explained (Rösch, *Ibid.*, 62, 928-936). Similar data for nonionic surfactants were developed. Types of structure occurring under varying conditions and in various solvents were described. Contrary to anionic surfactants, ethylene oxide condensates do not yield definable residues when air dried, and nonionic micelles were larger than those obtained from ionic surfactants (Rösch, *Ibid.*, 62, 1045-1049).

The constitutions and properties of surfactants were reviewed (Köbel et al., *Angew. Chem.* 73, 290-298). The action of surfactants at interfaces, and the consequences were reviewed (Moillet, *J. Oil & Colour Chemists' Assoc.* 42, 557-562). The influence of surfactant structure and of additives on detergency were reviewed (Jones, *Groupe recherches prod. superficiellement actifs, Colloq. 5e*, Paris, 1959, 127-139).

The McBain phase diagram for soap made from sulfur olive oil was studied and the boundaries of the isotropic and medium phases determined (Martinez and Caravaca, *Grasas y Aceites* 11, 132-138). The effects of free and oxidized fatty acids on the boundaries of neat soap and kettle wax phases were defined (*Ibid.*, 207-212).

Curves of intrinsic viscosity versus temperature of a polyoxyethylene surfactant had a maximum at a slightly lower temperature than cloud point in the two cases (Kuroiwa, *Kogyo Kagaku Zasshi*, 63, 1235-1238). Maximum viscoelasticities of several polyoxyethylene surfactants occurred at about 60% concentration (*Ibid.*, 1384-1387). Viscoelastic properties of several polyoxyethylene derivatives were determined (*Ibid.*, 2065-2067).

A discontinuity in viscosity, density, and cooling curves for a variety of anionic surfactants was found at 52 C (Fukutomi, *Oyo Butsuri* 30, 72-73). The rheological properties of polyethylene glycol-sorbitan oleate-water systems were studied using a rotation viscometer, as a function of water content, temperature, and shear strain (Vogt, *Fette, Seifen, Anstrichmittel* 63, 541-545). Permanent suspensions of oil-in-water polymer droplets was explained as a function of the yield value of the continuous water phase (Wolff and Meyer, *Soap Chem. Specialties* 37, No. 5, 131-135). Addition of 15-30% of aluminum or titanium alkoxides to aluminum soaps or naphthenates in organic solvents reduces viscosity (Kugler, *Czech.* 92,857).

A variety of surfactants adsorbed on the surface of copolymer lattices retarded deteriorative aging (Miura, *Kogyo Kagaku Zasshi* 64, 405-408). The mechanical stability of polystyrene latex was improved when anionic agents were adsorbed and nonionic agents with high HLB value were added (*Ibid.*, 408-411). Stability measurements as examined by turbidity after adding $CaCl_2$ to diluted latex showed that nonionic surfactants with high HLB were effective (*Ibid.*, 412-415). Whitening of latex films was less evident with anionic surfactants and nonionics of low HLB values (*Ibid.*, 416-419). Films of polyvinyl acetate, nitrocellulose and cellulose acetate were subjected to preferential wetting tests. Films more easily wetted by oil than water became more easily wetted by aqueous nonionic surfactant solutions than by oil, particularly when the hydrophobic radical was smaller (Kuroiwa, *Kogyo Kagaku Zasshi* 63, 2064-2065). Preferential wetting of polyvinyl chloride films by castor oil was lowered by surfactants, particularly when smaller hydrophilic and larger hydrophobic groups were present in the surfactant (Kuroiwa, *Kogyo Kagaku Zasshi* 64, 420-421).

Molecular distillation (centrifuge type) of commercial polyethylene glycol polymers yielded products which had a degree of polymerization curve agreeing with the theoretical curve of Flory. Other polyglycols and polyoxyethylene ethers and esters were distilled and the distillates analyzed (Masada et al., *Yukagaku* 7, 8-13). Counter current extraction data of polyoxyethylene adducts of dinonyl phenol had a wider mol wt distribution than predicted by the Flory-Poisson calculation, attributed to incomplete conversion to dinonylphenoxyethanol before subsequent monomer addition occurred (Mansfield et al., *JAOCs* 38, 289-291).

Radiotagged triglycerides were used to study their removal from glass surfaces (Harris and Anderson, *Am. Soc. Testing Materials, Spec. Tech. Publ.* No. 268, 20-26). Soil-removal studies with mixtures of surfactants and builders showed that nonionics were most effective when used in baths approaching their cloud points. Tripolyphosphate markedly improved soil removal by both anionic and nonionic surfactants (Harris et al., *JAOCs* 38, 123-127). Radiotagged protein and stearic acid from glass were more readily removed by water than tristearin; but at higher removal levels, radiotagged protein

becomes more difficult to remove. The shape of the protein soil removal curve lacks the sigmoid shape of the latter, suggesting either the lack of dependence upon critical micelle concentration, but more like an adsorption at an essentially single energetic level. The sigmoid shape suggests a van der Waals type of soil adsorption, followed at higher removal levels by a type of ion-exchange (Harris and Sataneck, *JAOCs* 38, 169-172). Radiotagged soils of the previous review were tested on a variety of substrates. Nylon, Teflon, methacrylate and stainless steel surfaces showed few soil adsorption sites and soil removal was of the ion-exchange type. Triglyceride soil showed a van der Waals type of adsorption on glass, steel and aluminum (*Ibid.*, 244-249).

Steel surfaces treated with glyceryl trioleate, oleic acid or octanoic acid soils showed maximum removal only with potassium laurate, all other surfactants tested performing best at multiples of cmc. Noted, was an increase in detergency with increase in concentration above cmc to a 90% removal level at which point the removal slope began to level off. The ratio of HLB values for several analogs was approximately equal to the fifth root of the ratio of their cmc values. Other relationships were discussed (Mankowich, *JAOCs* 38, 589-594).

The behavior of soap in water was investigated and showed special transitions at 50, 70 and 90°C. Heat treatment affected the ability of insoluble soap to swell but did not affect the final solubility (Dervichian, *Soap, Perfumery & Cos.* 10, 1061-1068).

The efflorescent fluffy coating on translucent soaps was found to have a lower melting point than the main body, and conversion to the methyl esters followed by gas chromatography showed enrichment of the fluffy coating to the extent that no saturated fatty acids were present (Prevat and Cabeza, *Rev. Franc. Corps Gras* 7, No. 5, 262-266).

Interfacial energy factors of surfactants were estimated by measurement of surface and interfacial tensions with organic liquids and the ϕ function of Girifalco and Good for the agents compared. The ϕ values for three organic liquids with ten surfactants were in close agreement, permitting the interfacial tension and free energy of adhesion to be estimated to an accuracy of about 1 erg/sq. cm. (Mankowich, *J. Chem. Eng. Data* 4, 254-256). The effect of chemisorption and van der Waals physical forces on soil retention, removal, and redeposition were discussed in a theoretical treatment. Other energy forces in detergent systems were described (Harris, *Soap Chem. Specialties* 37, No. 5, 68-71, 125; No. 6, 50-52; No. 7, 53-55).

Direct correlation between cmc, solubilization, and soil removal was demonstrated for a number of systems. Nonionic surfactants were excellent solubilizers for triolein correlating with their effective soil removal. Conversely neither sodium oleate nor tripolyphosphate effectively solubilized triolein, suggesting their mechanism of soil removal was by a displacement and emulsification mechanism (Ginn and Harris, *JAOCs* 38, 605-609).

Liquid crystals were formed at lower total active ingredient concentrations when monoesters of sucrose and tallow fatty acids were added to an aqueous solution of alkanolamine alkylarene sulfonate. In contrast, substitution of polyoxyethylene esters of fatty acids instead of the sucrose derivatives caused an increase in total concentration before liquid crystals formed (Osipow and Snell, *JAOCs* 38, 184-189). Water-insoluble long-chain polar compounds added to solutions of sodium alkylarene sulfonate resulted in the separation of a liquid-crystalline phase. Higher concentrations of water-soluble long-chain polar compounds required a 3 to 10 fold increase in the polar compound to produce liquid crystals. Deaggregation resulted in reduced foam and detergency, also decrease in Krafft temperature, viscosity and surface tension minima (Osipow and Snell, *Ibid.*, 38, 594-597).

PERFORMANCE AND USE TESTING

Performance characteristics of alkylbenzene sulfonates (mol wt 248-268) were studied for foaming and cleaning in dishwashing and laundering. Best balance was obtained by those in the middle range mol wt (Stewart, *Soap Chem. Specialties* 36, No. 12, 57-60, 154-157). The washing, foaming, and wetting activities of sucrose monourethans were investigated. Sucrose derivatives are advantageous in that they are completely nontoxic, and are destroyed by microorganisms (Ulsperger, *J. prakt. Chem.* 13, 90-94). Basic information dealing with structure, chemistry, and properties of quarteranaries and ampholytic surfactants was presented (Andersen, *Soap Chem. Specialties* 37, No. 4, 61-62, 99). The design and use of a specially constructed dynamic foam measurement de-

vice was described (Reich et al., *Soap Chem. Specialties* 37, No. 4, 55-57, 104). A technique was described for measuring detergent plasticity (Tschakert, *Soap Chem. Specialties* 37, No. 6, 157, 159, 161).

The functions of detergents in the washing process were described (Vader, *Chem. Weekblad* 56, 512-514). Measurement of the current flowing between two platinum electrodes coated with grease was used to evaluate cleaning ability (Oehler et al., *Deut. Textiltech.* 10, 589-593). Dairy detergents were tested by spreading milk on glass plates, drying, washing in detergent solution, staining with carbolfuchsin solution, and measuring light absorption spectrophotometrically at 540-560 m μ (Leesment, *Svenska Mejeriernas Riksförening U.P.A., Produkttek. Avdel. Meddel.* No. 58, 12 pp). Laundry detergent evaluations were made using calcium⁴⁵ tagged clay as the test soil (Hensley and Inks, *Am. Soc. Testing Materials, Spec. Tech. Publ.* No. 268, 27-39).

The effects on hand washing with detergents of varied compositions upon the lipid level of the skin and hands were determined (Lauren et al., *Acta Dermato-Venerol.* 39, No. 1, 35-40). Skin soiling and soil removing by detergents and their effects on the skin were described (Schwarz, *Fette, Seifen, Anstrichmittel* 62, 594-602). Results from arm immersion, human patch, repeated animal patch and water transmission tests for detergent mildness were applied to a variety of detergent products. Correlation among the four tests was good, and the arm immersion test appearing most sensitive (Justice et al., *Soap Chem. Specialties* 37, 53-56, 99, 101-102).

Carbon black dispersion was used to evaluate surfactants (Wagner, *Proc. Intern. Congr. Surface Activity, 2nd, London*, 4, 113-118). A high degree of dispersion of carbon black occurred only in the presence of adsorbing long-chain amphiphatic molecules, but calcium ions cause agglomeration (Peper and Rosano, *JAOCs* 38, 500-504). The redeposition of hydrophobic pigments by four electrolytes in surfactant solutions was measured, and various results were discussed (Vaeck, *Fette, Seifen, Anstrichmittel* 62, 846-853). The electrophoretic velocity and sedimentation rates as functions of concentration showed an inverse relation (Briant and Bernelin, *Group recherches prod. superficiellement actifs Colloq.*, 5e, Paris 1959, 27-36).

Foaming and foam stability were measured in a simple apparatus (Photakis and Schaläpfer, *Melliand Textilber.* 42, 945-946).

Physical and functional tests for dry cleaning detergents were presented (Weeks and Lewis, *Soap Chem. Specialties* 36, No. 9, 65-68; No. 10, 50, 105, 107).

The stability of oil-in water emulsions was measured by determining the degree of phase separation upon the application of a known centrifugal force. Maximum emulsion stability often corresponded to minimum surface tension and at an HLB value of 9.5 (Wachs and Reusche, *Fette, Seifen, Anstrichmittel* 62, 803-810).

Miscellaneous

The latest revision of surfactants was issued for sale (McCutcheon, *Soap Chem. Specialties* 36, No. 11, 54-62; No. 12, 64-72; 37, No. 1, 51-58). The economic information for the U. S. surfactant industry was reviewed, a classification given, and the effect of structural changes on properties noted (Ayo et al., *Soap Chem. Specialties* 37, No. 5, 59-61; No. 6, 54-57, 111, 113).

Various types of household detergents, the trends in this field, and developments such as monofatty acid esters of sucrose, optical bleaches, and syndet bars were discussed (Snell and Snell, *Soap Chem. Specialties*, 36, No. 9, 55-58). Recent advances were noted in surfactant manufacture (Amen-de, *Fette, Seifen, Anstrichmittel* 63, 441-445), and recent surfactant chemistry was reviewed (Oda, *Yuki Gosei Kagaku Kyokaiishi* 18, 874-878). A lecture was concerned with the development and importance of the surfactant industry (Hagge, *Fette, Seifen, Anstrichmittel* 63, 221-225).

A check-list of the principal considerations involved in marketing a new surfactant was given (Pacifico, *Soap Chem. Specialties* 37, No. 3, 52-55, 109).

Fluorocarbon surfactants were reviewed (Komori, *Yakagaku* 10, 2-5), as were industrial metal cleaners (Price, *Soap Chem. Specialties* 36, No. 12, 61-64, 255-256).

Triethanolamine soaps were considered as emulsifiers (Failla, *Am. Perfumer Aromat.* 76, No. 3, 39-42).

The comparative usefulness of the classes of surfactants was reviewed on the basis of their use in the catering industry, with particular attention to their effect on bacteria (Hobbs et al., *J. Appl. Bacteriol.* 23, 350-358).

PRODUCTS (EXCEPTING DETERGENTS)

EDIBLE, PHARMACEUTICAL, AND COSMETIC
FAT PRODUCTS

Variations in milk fat and the solids-not-fat percentage were shown to be related to the age of the cow, stage of lactation, and the month of the year (Johnson et al., *J. Dairy Sci.*, 44, 658). The level of fat required for maximum acceptability was shown to be a function of the solids content of the milk. At 12–15% total solids, milk containing 2–3% fat was found to be more acceptable than milk containing 4% fat. No significant flavor differences were noted for 2–3% fat content in milk containing 11 or 12% solids, but these samples were more acceptable than unfortified milk containing 3.7% fat and 9.2% nonfat milk solids (Wahid-Ul-Hamid and Manus, *J. Dairy Sci.*, 43, 1430). A review discussed the nutritional quality of milk in which the fat of the whole milk is replaced by coconut oil, and pointed out that milk fat carries with it important milk nutrients, not present in skim milk or coconut oil. Therefore, milk fat rates higher nutritionally than coconut oil during the growth period and when the diet otherwise is marginal (Rice, *J. Agr. Food Chem.*, 8, 488). All of the major and many of the minor fatty acids of milk fats were determined by a specially adapted gas-liquid chromatography procedure (Smith, *J. Dairy Sci.*, 44, 607). GLC methods were also used to show high levels of *trans* octadecenoic acids and an increase of C-18 acids in summer milk at the expense of palmitic acid (Patton et al., *J. Dairy Sci.*, 43, 1187). *Trans* acids in cows' milk were found to range from 6.3 to 9% in summer and from 0.1 to 1.7% in winter, while the *trans* acid content of human milk varied only from 0–4% (Kaufman et al., *Fette, Seifen, Anstrichmittel* 63, 261). Using gas-liquid chromatography and the mercaptoacetic acid method for the determination of saturated triglycerides in milk, it was concluded that the major saturated fatty acids of milk show a limited random distribution (Boatman et al., *J. Dairy Sci.*, 44, 544). Acid and non-acid volumetric tests for butter fat in whole milk were compared (O'Dell, *J. Dairy Sci.*, 44, 47). Wettability measurements on milk powders prepared from homogenized mixtures of butter oil and condensed skim milk showed that the monoglycerides (Myverol) had a greater effect on wettability when they were incorporated in the nonfat portion of the milk. Span and Tween preparations exerted a more pronounced effect when they were incorporated in the fat portion of the milk (Baker and Samuels, *J. Dairy Sci.*, 44, 407). Flavor constituents in the low temperature vacuum distillate of reconstituted dry whole milks, were found to be largely carbonyl in nature (Parks and Patton, *J. Dairy Sci.*, 44, 1). Another study showed that aldehydes bound as enol ethers and located mostly in the alpha position of glycerol could be isolated from non-phosphatide lipids of milk fat, beef tallow and ox heart (Schogt et al., *J. Lipid Research* 1, 446).

Butter samples were evaluated for spreadability and hardness, comparing results of a consumer panel and of a device called a Consistometer. Desirable butter from the consumers' standpoint showed a range on the Consistometer of 400 to 900 g resistance to the knife used to measure spreadability and 140–200 g resistance to the wire used to measure hardness (Kapsalis et al., *J. Dairy Sci.*, 11, 1560). Pancreatic lipase hydrolysis and gas chromatographic analysis of 2 samples of butter fat showed that saturated and unsaturated acyl groups appear to be distributed intermolecularly at random, but tend to assume specific positions intramolecularly. It was concluded that saturates and unsaturates in butter fat are associated as S₁, S₂U, SU₂ and U₃ in proportions which can be specified by probability laws (Ast and Vander Wal, *JAOCs* 38, 67). The first odd-numbered unsaturated fatty acid identified in butter fat, *cis*-Δ⁹-heptadecenoic acid was isolated in a yield of approximately 0.06% of the total weight of the fatty acids (Hansen et al., *Biochem. J.*, 77, 64). As little as 7% of hydrogenated fat in butter was detected by infrared determination of increases in isolated *trans* double bonds introduced in the hydrogenated fat (Bartlett and Chapman, *J. Agr. Food Chem.*, 9, 50). The feasibility of flavoring Canadian butter with starter distillate and a commercial preparation of synthetic diacetyl was investigated. Starter distillate butters were preferred by a taste panel, and 0.50 oz of distillate per 100 lb of fat was optimum. Peroxide values indicated that the keeping quality of the butter was unaffected by either flavoring (Riel and Gibson, *Food Technol.*, 15, 137).

Methods for making margarine with or without occluded gas were patented. By a whipping procedure, 15 to 40% of inert gas by volume can be uniformly and finely dispersed in the margarine (Melnick, *U. S. 2,970,917*). By superheating a liquid margarine to 15 to 40F below the setting point of the

fat ingredient, and then working to dissipate at least 20% of the potential titer heat due to fat crystallization, a margarine product substantially free of occluded gas can be produced (Melnick, *U. S. 2,973,269*). Flavor stabilization was achieved in salted margarine by incorporating an edible citric acid component and an edible ethylenediaminetetraacetic acid component (Melnick, *U. S. 2,983,615*). An oil suitable for margarine manufacture was prepared by co-randomizing a mixture of 40-60 parts palm oil (or tallow, hydrogenated whale, fish or vegetable oil), and from 60 to 35 parts of a coconut-type oil. Then 1–30% by wt of total oil of an unrandomized oil of the coconut type is added (Lindsey, *U. S. 2,996,388*). In another procedure for margarine manufacture, an emulsion of fat and liquid milk, in which the fat is in the dispersed phase, was incorporated into a melted edible fat. The mixture was then chilled and worked to disperse the fat from the emulsion as globules coated with non-fat milk solids (North et al., *U. S. 2,997,396*). Linoleic acid content of eleven commercial margarines was found to vary from 8 to 34 g per 100 g of margarine (Ostwald, *J. Am. Dietet. Assoc.* 39, 313).

A liquid shortening comprising a stable suspension of discrete particles of solid fats in oil in a temperature range of 60–110F was prepared by melting the oil completely, converting to the beta prime form, then heating to convert to the beta crystalline form (Payne and Seybert, *U. S. 2,999,022*). However, in a study of the baking qualities of sodium methoxide treated lards, elimination of beta crystal properties was found necessary to retain desirable characteristics (Wiedermann et al., *JAOCs*, 38, 389). The course of the reaction during sodium methoxide treatment of lard was described as taking place in three stages: (1) Reaction of the sodium methoxide with the fat to form an active catalyst; (2) crystal modification; (3) several stages of interesterification (Weiss et al., *JAOCs*, 38, 369). Differential cooling curve techniques were applied to a study of the various degrees of modification of lard and compared with the data for some other types of glyceride mixtures (Jacobson et al., *JAOCs*, 38, 399). An improved edible shortening was produced by treating the triglyceride with itaconic acid in the presence of an interesterification catalyst, under conditions leading to rearrangement of the triglyceride and substitution of some of the ethylene carboxylic acid radical of the itaconic acid for some of the triglyceride fatty acid radicals (Gleason, *U. S. 2,966,412*). A mixture of glycerides containing a minor amount of short chain acid groups added in small amounts to tallow was claimed to form a shortening, having a wide plastic range and good creaming and cake baking characteristics (Weiss, *U. S. 2,966,411*). Improved shortenings were also prepared by molecularly rearranging a triglyceride in the presence of an interesterification catalyst and adding 0.1 to 3% by wt of a hydroxycarboxylic acid to cause substitution of the hydroxy acid for some of the fatty acid radicals originally in the triglyceride fat (Gleason, *U. S. 2,970,055*).

Among emulsifier systems patented for shortening compositions were: a combination of a surface active agent and a monoglyceride in a liquid edible oil (Schroeder and Houser, *U. S. 2,968,564*); partial esters of fatty acids with a hexahydric alcohol or anhydride, a polyoxyalkylene derivative of such a partial ester, or an ester-ether resulting from the reaction of fatty acids with alkylene oxides, and an ester of glycerine and a hydroxy acid (Houser, *U. S. 2,968,562*); the combination described in *U. S. 2,968,562* plus an edible monoglyceride (Houser, *U. S. 2,968,563*); mixed glycerides of lactic acid and C₁₂ to C₂₀ fatty acids, at least half of which are palmitic acid, plus acidic emulsifiers such as acidic cetyl citrate, acidic stearyl lactyl tartrate, the acidic stearyl alcohol ester of diacetyl tartaric acid or an acidic ester of a monoglyceride of a C₁₈ aliphatic hydrocarbon monocarboxylic acid, and diacetyl tartaric acid (Julian et al., *U. S. 3,004,853*); hexitol and hexitan partial esters of a C₁₂₋₂₂ fatty acid and lactic acid (Radlove, *U. S. 2,996,387*); and the diglyceride reaction product of glycerine, higher fatty acids containing at least 60% by wt of myristic acid, and an alkyl monohydroxy monocarboxylic acid of 2–6 carbon atoms (Chang et al., *U. S. 2,966,410*).

Solid monoglycerides of saturated fatty acids having a chain length greater than 18 carbon atoms were incorporated into a fluid shortening composition (Handschumaker and Hoyer, *U. S. 2,999,755*). Shortening for cake mixes included 0.5% of an acyl lactic acid containing 1 to 6 lactyl groups (Thompson and Buddemeyer, *U. S. 2,973,086*). An emulsifier was included in the shortening of a batter suitable for refrigerated storage. It was composed of a lower hydroxycarboxylic acid fatty acid ester of an edible polyhydric alcohol, in which there was also at least one mole of fatty acid of 12–22 carbon atoms esterified per mol of polyhydric alcohol (Cochran et al., *U. S. 2,982,662*). A method was described

for analyzing shortenings containing glycerol lactopalmitates and lactostearates by determination of water insoluble combined lactic acid (Fett, *JAOCs*, 38, 447). NGDA in lard was determined by extracting a petroleum ether solution with 50% methanol, adding silver nitrate and buffer and complexometrically determining the separated precipitate of reduced silver (Sedlacek, *Fette, Seifen, Anstrichmittel*, 62, 669).

Baking and frying fats were the largest single domestic outlets for fats and oils during 1955-1959. Consumption of fats and oils in soaps and in paints and varnishes fell off sharply during this period, while gains were experienced in consumption in animal feeds and plasticizers (Anon., *Chem. Eng.*, 67 [24], 90). The method of caring for frying fat was shown to markedly affect its useful life. Frying life was more than doubled by filtering, storing in a covered metal container at 2-5 C or at 20-25 C and adding 20% of fresh fat each 8 hr frying period (Rust and Harrison, *Food Technol.*, 14, 605). The smoke point of frying oils was raised from 15 to 35 F during a relatively large number of fryings by dispersing methyl or ethyl siloxanes in the fatty glyceride (Babayan, *U.S. 2,998,319*). Glyceride oils were also found to be protected against darkening, nutritional losses and viscosity increases during prolonged heating at cooking temperatures by addition of at least 0.001% of alpha sitosterols (Chang and Mone, *U.S. 2,966,413*). Dimers in oxidized fats were determined by a liquid-partition chromatographic method (Frankel et al., *JAOCs*, 38, 130). Carbonyl content of thermally oxidized fats was determined using hydroxylamine hydrochloride as reagent and n-octyl alcohol as solvent (Balero et al., *JAOCs*, 38, 689). Studies of the physiological properties of heated animal and vegetable fats showed that carbonyl compounds which form, are deposited in rat carcass fat (Wurziger and Ostertag, *Fette, Seifen, Anstrichmittel*, 62, 895). Two isomeric 2,4-hepta- and 2,4-decadienals, formed from linoleic and linolenic acids, were isolated by gas-liquid chromatography from the volatile decomposition products of soybean oil (Hoffman, *JAOCs*, 38, 31).

Studies of the volatile pyrolysis products of lean and fat beef and pork, showed flavor differences are contributed by the fat (Hornstein and Crowe, *J. Agr. Food Chem.*, 8, 494). Irradiation of beef with doses of 25,000 to 100,000 rads at chilling temperatures to retard microbial spoilage, caused accelerated oxidation of fatty tissue in the region near surfaces exposed to air (Lea et al., *J. Sci. Food Agr.*, 11, 690). A specially processed dry mixture of 0.2-25 parts by wt of protein, 0.2-50 parts of sugar and 100 parts of a fatty glyceride was patented as a stabilizer for edible fats (Williams et al., *U.S. 3,001,878*). Included in a frozen stabilized dessert composition were 2-22% by wt of a vegetable oil having a pour point lower than the freezing point of water, and an unsaturated fatty acid content of more than 70%, 2-15% of nonfat milk solids or non-milk protein solids, 10-25% of sugar solids other than lactose of non-fat milk solids, and 45-75% water (Peat, *U.S. 3,003,882*). In a mayonnaise composition based on soybean oil, the amount of soybean oil was adjusted according to the iodine value of the oil (Melnick and Akerboom, *U.S. 2,983,618*). The presence of more than 5% stearine in cottonseed oil was detected by dissolving 5 ml of oil in 10 ml of hexane and chilling at 0C for 20 hr (Macchi and Crespo, *Rev. Arg. Grasas y Aceites*, 3, 3). Specifications for a deodorized hydrogenated vegetable oil for continuous frying of potato slices included an I. V. of 75 to 94, a melting point of 80-95F, and a setting point of 55-65F (Gooding and Melnick, *U.S. 2,973,268*).

Chromatographic methods were used to show the presence in olive oil of oleanolic acid, 3-beta-hydroxyolean-12-en-28-oic acid, and a normal dihydroxy triterpenoid acid (Vioque and Morris, *JAOCs*, 38, 485), and 3.6% of epoxy acids of which the major component was trans-9,10-epoxystearic acid, and 6% of a monohydroxy acid (Vioque et al., *JAOCs*, 38, 489). Chromatographic separation and detection of the sterols present in fats were used to distinguish animal from vegetable fats (Hatzopoulos, *Rev. Franc. Corp. Gras*, 7, 575). Gas-liquid chromatography was also used in the identification of 3-cis-hexenal as the source of the green bean odor in oxidized soybean oil (Hoffman, *JAOCs*, 38, 1), and to separate some 27 ether soluble neutral components from bread pre-ferment liquid (Smith and Coffman, *Anal. Chem.*, 13, 1733). Among the latter, identified by IR spectroscopy and mass spectrometry, were levo and meso isomers of 2,3-butanediol, ethyl formate, gamma-butyrolactone, the monoacetate of 1,3-propanediol and beta-phenylethanol. A rapid and reproducible method for determination of lipids in brewing adjunct cereals was reported (Haas and Fleischman, *Cereal Chem.*, 38, 198). Low temperature extraction of wheat flour lipids and gradient elution from silicic acid effected separation of sterol ester and triglycerides, phosphatidylethanolamines, lecithins, lysolecithins, and ethanolamine-containing lipids different from the phos-

phatidylethanolamines (Wren and Elliston, *Chem. & Ind.*, 1961, 80). Flavor components isolated from fats and oils by countercurrent contact of the oil with steam, condensation of the steam volatiles, and liquid-liquid extraction of the condensate with diethyl ether were found to give bland coconut oil, the flavor of reverted soybean oil (Chang, *JAOCs*, 38, 669). Countercurrent distribution was used to separate the fractions responsible for the two types of spectra characteristic of crude cottonseed oils. In the hydrophilic phase were gossypol and pigments absorbing below 375 m μ . These were trapped by molecular sieve No. 13X and appeared in the liquid fraction on crystallization from acetone at -63C. In the hydrophobic phase were another group of pigments absorbing at 375-400 m μ , which were not admitted by molecular crystallization (Verberg et al., *JAOCs*, 38, 33). Adsorption of the fixed red pigments from refined, off-color cottonseed oil by several adsorbents followed the Freundlich adsorption isotherm (Pons et al., *JAOCs*, 38, 104). Extraction of raw cottonseed meats with an acetone-petroleum ether-water mixture was found to preserve lysine and reduce the total gossypol in the meats (King et al., *JAOCs*, 38, 19). Fatty acid composition of cottonseed oil was found to be constant at all stages of hexane extraction of flaked prime cottonseed meats (Arnold and Choudhury, *JAOCs*, 38, 87).

Cocoa butter glycerides were separated into 43 fractions by thermal gradient crystallization and it was concluded that the composition appears to agree with that predicted for restricted random distribution (Jones and Hammond, *JAOCs*, 38, 69). Evidence for random distribution of palmitic and stearic acids on the 1 and 3 positions of glycerol with oleic acid in the 2 position was obtained by a study of natural, interesterified, and synthetic cocoa butters. Complete randomization by interesterification greatly altered the properties of the cocoa butter, but a glyceride synthesized according to the 1,3-random-palmito-stearo-2-olein pattern, closely resembled natural cocoa butter (Dutton et al., *JAOCs*, 38, 96). "Bloom" crystals were shown by paper chromatography to contain the same 3 glycerides as the original cocoa butter, but with a smaller proportion of oleodipalmitin (Steiner and Bonar, *J. Sci. Food Agr.*, 12, 247). A bloom inhibited chocolate was produced by adding up to 5% of a mixture of triglycerides based on the ratio of 2 mole of lauric acid, 1.2 mole of myristic acid and 2 mole of palmitic acid (Duck, *U.S. 2,979,407*). Temperature was found to be a direct factor in decreasing crystalline organization and increasing amorphous character of purified cocoa butter during oxidation (Sterling, *Food Research*, 25, 770). Dilatometric properties of various oleodistearins and oleodipalmitins were studied as part of an investigation of synthetics for confectionery fats (Landmann et al., *JAOCs*, 38, 681).

Cocoa-butter-like fat was prepared on a pilot plant scale by interesterification of hydrogenated cottonseed oil and a triolein product or olive oil followed by fractional crystallization from acetone at 20-28C and at 0C (Spadaro et al., *JAOCs*, 38, 461). The resulting fats contained varying amounts of glycerides melting above 37C, which caused the fat to thicken too much when used in chocolate-type compositions. These were removed by an additional crystallization to obtain an acceptable cocoa butter substitute (Landman et al., *JAOCs*, 38, 466). Cocoa butter or a Borneo tallow type fat was mixed with at least 5% by wt of a palm oil fraction having an I. V. not greater than 45, a dilation at 20C of not less than 1000, and a softening point of 30 to 45C to form a cocoa butter substitute (Best et al., *U.S. 2,975,060*). Preparation of the palm oil suitable for use as a cocoa butter substitute as described above was also described in another patent (Paul and Crossley, *U.S. 2,975,063*). Other materials suggested for extending or replacing cocoa butter included a tallow fraction (Soeters et al., *U.S. 2,975,062*), a lard fraction (Soeters et al., *U.S. 2,975,061*), a mixed fatty acid diester of propylene in which the acyl radicals are a mixture of oleyl and palmitoyl or stearoyl radicals (Alsop and Bell, *U.S. 2,993,063*), sucrose esters of fatty acids having 10-24 carbon atoms (Babayan and Comes, *U.S. 2,999,023*), and a triglyceride containing only fatty acids of 16 and 18 carbon atoms comprising 25-55% saturated fatty acids, 30-50% trans monothenoic acids, and 15-40% cis monothenoic acids (Cochran et al., *U.S. 2,972,541*).

A carrier for a therapeutic agent was described as containing equal parts of glyceryl monostearate and gum karaya combined with an equal weight of a solid, nontoxic water insoluble material (Nash and Jeffries, *U.S. 2,993,836*). Safflower oil, glycerin and lecithin were patented as components of an aqueous medium for intravenous administration (Zilversmit, *U.S. 2,972,565*). An alcohol solution of an oil soluble dye and a triglyceride composed of a 2:1 mixture of caprylic and capric acids and 0-5% of approximately equal proportions of caproic and lauric acids (Barsky and Babayan, *U.S.*

2,988,483) was patented as a carrier for vitamins and antibiotics (Barsky and Babayan, *U. S. 2,988,484*).

Sugar esters and sucroglycerides prepared by a transesterification procedure were suggested as potentially useful raw materials in cosmetics (Noble, *Drug and Cosmetic Ind.*, 89, 34). A formulation for a soap-free opaque cream shampoo included sodium alkyl glyceryl ether sulfonate, N-acyl secosine, sodium N-acyl sarcosinate, or mixtures, inorganic salts, and water (Parran et al., *U. S. 2,979,465*). A cream base for general use included cetyl or stearyl alcohol, or mixtures of the two, fatty alcohol sulfonate as an emulsifier, oleic acid oleyl ester, water, *Oleum hyperici*, urea and citric acid (Riethmiller, *U. S. 2,987,446*).

EMULSIFIERS

Emulsifiability and solvent selection of carnauba wax is associated with the presence of long-oxylated long-chain esters which comprise a majority of the molecules (Prince, *Soap, Chem. Specialties*, 36 [9], 103). Stable emulsions of linoleic acid in buffered solutions were prepared by sonic vibrations, and solubility data and conductivity values obtained (Mabrouk and Dugan, *JAOCs*, 38, 9). Monoglycerides were found to decrease interfacial tension to some extent in lipolyzed milk fat-water systems (Duthie et al., *J. Dairy Sci.*, 44, 401). Glycerides and fatty acid composition of 20 commercial monoglyceride ice cream emulsifiers were determined (Jensen et al., *J. Dairy Sci.*, 44, 1057). To prepare a spreadable and reconstitutable emulsified product, the fatty component of fresh coconut juice was isolated by gravitational separation to retain the fatty components in the dispersed phase (Wen, *U. S. 2,981,627*). The product of the reaction between beta-propiolactone and fatty acids of 6 to 22 carbon atoms was patented as an emulsifier for glyceride shortening compositions (Young and Spitzmueller, *U. S. 2,963,371*). Emulsifiers wholly soluble at 25 at a 4% level in liquid edible, triglyceride shortening oils were prepared by reacting together under esterifying conditions molar equivalents each of glycerol and a fatty acid mixture composed of at least 50% by wt of palmitic acid, the remainder being saturated fatty acids of 12-20 carbon atoms, plus up to 3 molar equivalents of monohydroxy monocarboxylic acids of 2-4 carbons (Radlove et al., *U. S. 2,957,932*). In a study of fluid shortening media, it was shown that factors affecting emulsion viscosity are monoglyceride level and hardness, the ratio of sorbitan monostearate and their level, and the shortening basestock used (Geisler, *JAOCs*, 38, 306). New non-ionic emulsifying agents, the polyoxyethylated methyl glucoside esters of saturated and unsaturated fatty acids were found to lower the surface tension of water appreciably in concentrations as low as 0.01% (Otey et al., *JAOCs*, 38, 517). Equal parts of glyoxalidine and a condensation product of glyceride oil with an alkylolamine were used as an emulsifier for waxes (Fronmuller and Mirra, *U. S. 2,974,106*). Monooleates and monolaurates of polyethyleneglycols were dispersing agents for zinc stearate in an aqueous, adherent, non-dusting lubricant coating composition for plastic surfaces (Price, *U. S. 2,965,539*). There was an extensive investigation of the nature of the emulsion, alpechin, obtained in crushing olives (Marquez, *Grasas y Aceites*, 11, 83).

ESTERS, ACIDS, ALCOHOLS AND OTHER FAT DERIVATIVES

A procedure for the synthesis of mixed acid 1,2-diglycerides in any one of the four theoretically possible forms was applied to the synthesis of D-1-stearoyl-2-oleoylglycerol and D-1-oleoyl-2-stearoylglycerol (Buchnea and Baer, *J. Lipid Research*, 1, 405). Diglycerides were also formed by treating fat with 0.3 to 1.0% glycerine in the presence of 0.02 to 1.0% of a catalyst (Seestrom et al., *U. S. 2,999,021*). Diglycerol synthesized from diallyl ether by $KMnO_4$ oxidation, or by the action of sodium bicarbonate on di(2-hydroxy-3-chloropropyl) ether, was used in the preparation of stearyl, lauroyl, and palmitoyl derivatives (Kaufmann and Forster, *Fette, Seifen, Anstrichmittel*, 62, 796). Chemical and physical properties were reported for 2,3-dibutyro, 2,3-di-isobutyro-, and 2,3-di-isovalero-1-olein prepared from the corresponding acid chloride and 1-mono-olein (Taufel et al., *Fette, Seifen, Anstrichmittel*, 62, 926). Glyceride structure of fats was determined by quantitative oxidation of the unsaturated acids to the corresponding dicarboxylic acids, separation of these by liquid-liquid partition into a fraction containing no dicarboxylic acid or one dicarboxylic acid and a second fraction containing 2 or 3 dicarboxylic acids, and further characterizing these fractions by lipase hydrolysis and gas chromatography (Youngs, *JAOCs*, 38, 62). In a somewhat similar micromethod for determination of component mono-, di-, and triglycerides, the

double bonds were ozonized, the ozonides reduced catalytically, and the resulting glyceryl residues separated by thin-layer chromatography (Privett and Blank, *J. Lipid Research*, 2, 37). Separation of mixtures of mono-, di-, and triglycerides, hydroxy-, epoxy-, and episulfido-fatty acids, aldehydes, and amides by thin-layer chromatography was studied (Kaufmann and Makus, *Fette, Seifen, Anstrichmittel*, 62, 1014). In a similar study of mixtures incorporating hydrocarbons, cholesterol esters and free sterols with glycerides, chromatographic separation was effected on activated magnesium silicate (Florisil) (Carroll, *J. Lipid Research*, 2, 135). Glycerides of mixed fatty acid chains were separated on glass fiber paper using solvents consisting of 2% and 5% ether in iso-octane (Ory, *J. Chromatography*, 5, 153). Increasing amounts of ethyl ether in n-hexane were used to elute mixed-chain-length glycerides from a silicic acid chromatographic column, and it was found that glycerides containing short chain acids or unsaturated acids were most strongly adsorbed (Sahasrabudhe and Chapman, *JAOCs*, 38, 88). Comparing molecular distillation and thin-layer chromatography as methods of separation of mono-, di-, and triglycerides it was concluded thin-layer chromatography is most effective (Privett et al., *JAOCs*, 38, 312). Analysis of glycerides by high temperature gas-liquid partition chromatography was reviewed (Huebner, *JAOCs*, 38, 628). Other chromatographic analyses of glycerides included a review of thin-layer chromatography (Mangold, *JAOCs*, 38, 708), and a discussion of the monitoring of radioactive eluates from chromatography and countercurrent distribution (Dutton, *JAOCs*, 38, 631).

Kaufman and co-workers reported that spectra of fats and synthetic glycerides with only saturated fatty acids exhibit absorption at 10.33μ which can be mistaken for trans unsaturation. This absorption was also observed in the esters of saturated fatty acids with polyalcohols (Kaufmann et al., *Fette, Seifen, Anstrichmittel*, 63, 8). This spurious absorption by triglycerides can be eliminated by a correction of data (Firestone and Villadelmar, *J. Assoc. Offic. Agr. Chemists*, 44, 459). Applications of infrared absorption spectroscopy and near infrared spectroscopy were reviewed (O'Connor, *JAOCs*, 38, 641). Barcelo also published a review (*Barcelo, Grasas y Aceites*, 11, 34).

The rate of isomerization of 2-monoglycerides to 1-monoglycerides in mixtures stored in the solid state was found to increase as the chain length of the acyl group decreased (Aylward and Wood, *Chem. & Ind.*, 1960, 1442). A monoglyceride-rich tung oil product was prepared on a large scale, but analysis for monoglyceride was complicated by interference by triene conjugation and by components other than simple monoglycerides (Eaves et al., *JAOCs*, 38, 443). Hydrolysis of sunflower oil in a homogenous phase was found to lead to formation of monoglycerides in amounts indicating an equilibrium must exist between hydrolysis and esterification during the splitting process (Peredi, *Fette, Seifen, Anstrichmittel*, 62, 1034). A glycerol fatty acid partial ester composition containing at least 75% by wt of monoglyceride formed a firm, clear gel with water (Brokaw and Lyman, *U. S. 2,976,251*).

Techniques were described for avoiding loss of lecithin at the point of origin during quantitative separation of phospholipids on silicic acid impregnated filter paper (Zieve et al., *Proc. Soc. Exptl. Biol. Med.*, 105, 508), for qualitative and quantitative isolation and analysis of phosphatides and glycolipids using thin layer and paper chromatography, countercurrent distribution and infrared spectroscopy (Wagner, *Fette, Seifen, Anstrichmittel*, 62, 1115); and for saponification and hydrogenation of lecithin on paper preparatory to paper chromatographic analysis of its components (Kaufmann and Wessels, *Fette, Seifen, Anstrichmittel*, 62, 1020). Procedures were also described for determination of cholesterol and squalene in biological mixtures (O'Neill and Gershbein, *Anal. Chem.*, 33, 182), for separation of cholesterol esters and triglycerides on silicic acid columns by elution with mixtures of benzene in hexane (Hornig et al., *J. Lipid Research*, 1, 482), and for separation of vitamins A and D, and cholesterol, on polytetrafluoroethylene packed column (Arcus and Dunckley, *J. Chromatography*, 5, 272).

A eutectic product identifiable as commercial stearic acid was obtained by sub-atmospheric distillation of a mixture of fatty acids compounded to contain a maximum of 75 parts stearic per 100 parts palmitic-stearic and a maximum of 58 parts of palmitic acid per 100 parts of the mixture (McGuine and Feldpush, *U. S. 2,985,674*). Oleic ricinoleic, palmitic-oleic, and palmitic-stearic acid mixtures were shown to vary from the expected vapor-liquid equilibria calculated according to the Raoult-Dalton law (Hollo and Lengyel, *Fette, Seifen, Anstrichmittel*, 62, 913). Odorous substances were removed from fatty acids by treating the acids with acetic anhydride to form fatty anhydrides and distilling off excess acetic an-

hydride, acetic acid which was formed and the odorous substances (Ward, *U.S. 2,981,744*). An apparatus was described for isolation of volatile constituents from fats and oils by vacuum degassing (DeBruyn and Schogt, *JAOCs*, 38, 40). A method was also developed for determination of steam volatile fatty acids by gas-liquid chromatography (Gehrke and Lamkin, *J. Agr. Food Chem.*, 9, 85). To separate fatty acids from oxidized fish oils, an aqueous acid solution was added, the resulting mass was heated and treated with potassium permanganate solution; and after alkalizing, a water soluble aluminum salt was added to form aluminum soaps (Buloff, *U.S. 2,972,624*). Hydroperoxides in autoxidized fatty acids and methyl esters were determined chromatographically and results compared with data obtained by determining peroxide values or diene conjugation (Frankel et al., *JAOCs*, 38, 134).

Fatty acids having 10 to 18 carbon atoms in the chain were separated from each other by countercurrent distribution using petroleum ether as the upper layer and a 9 to 1 ratio of dimethylsulfoxide to 1-octanol as the lower layer (Will, *Anal. Chem.*, 33, 647). Dibasic acids of 6 to 12 carbon atoms were separated from each other in the presence of monobasic acids by a modification of the paper chromatographic technique of Zbinovsky (Occolomitz, *J. Chromatography*, 5, 373). Propylene glycol supported on silicic acid was used in the partition chromatographic separation of the short chain fatty acids from formic through capric (Gordillo and Montes, *Rev. Arg. Grasas y Aceites*, 3, 31). Several procedures for separation and analysis of fatty acids and other lipids were reviewed and compared (Fontell et al., *J. Lipid Research*, 1, 391). Reviews on crystallization of fatty acids (Schlenk, *JAOCs*, 38, 728) and chemical means of determination of fatty acid structure (Stein, *JAOCs*, 38, 636) were published. Methods were presented for determination of fatty acids with isolated double bonds in the presence of conjugated fatty acids using ultraviolet spectra (Schauenstein and Benedikt, *Fette, Seifen, Anstrichmittel*, 62, 687); and for infrared determination of trans unsaturation in some 35 different fatty materials including triglycerides, free fatty acids, and methyl esters (*Jart, Oleagineux*, 16, 101). Long chain fluoro-fatty acids were separated from the reaction mixture and purified using reverse phase chromatography on cellulose powder treated with liquid paraffin (Hall, *J. Chromatography* 5, 93). A colorimetric method for determining fat acidity in grain was based upon the reaction between the fatty acids and aqueous cupric acetate in benzene solution to form a blue benzene-soluble soap (Baker, *Cereal Chem.*, 38, 7). The various analyses relating to the degree of hydrolysis of fats were correlated with the mono-, di-, and triglyceride content (Ceballos, *Grasas y Aceites*, 11, 79). Refining losses were determined by "sodium analysis" of the flow stream and substitution of sodium values for each component in an equation (Crauer and Sullivan, *JAOCs*, 38, 172). In extraction studies, it was found that as the residual oil content of soybean meal decreased, the refining loss, phospholipid content, and color of the extracted oil increased with no significant change in other properties (Arnold et al., *JAOCs*, 38, 336). A process incorporating lignin in vegetable oil wash waters was reported to increase recovery of fatty materials and decrease BOD of the effluent (Allen and Wack, *U.S. 2,993,006*). Fatty acid content of soapstocks was determined by acidulation with hydrochloric acid and titration with sodium hydroxide to a bromphenol endpoint and a phenolphthalein endpoint (Bastanski, *Rev. Arg. Grasas y Aceites*, 3, 27). Use of ion exchange resins for separation of free fatty acids from fats, separation of fatty acid mixtures, separation of glycerine and various other processes were reviewed (Ollero and Soto, *Grasas y Aceites*, 11, 81). An evaluation of "snake-cage" amphoteric resins, produced by Dow, for separation of sodium chloride from glycerine showed ion retardation was slightly cheaper than the ion exclusion process (Hatch and Smith, *JAOCs*, 38, 470). In studies of the selective hydrolysability of rice bran lipase, palmitic acid was most rapidly hydrolyzed, linoleic least rapidly, and oleic was hydrolyzed at an intermediate rate (Kimura, *Yukagaku*, 10, 136). Inactivation of Twitchell reagent by the so-called negative catalysts in rancid oils was studied (Kasino et al., *Kogyo Kagaku Zasshi*, 64, 311).

Lead soaps of stearic, palmitic, and oleic acids were patented as stabilizers for vinyl chloride resin compositions (Kebrieh, *U.S. 3,002,943*). Alkyllead compounds were stabilized by incorporating small amounts of monocarboxylic acids ranging in chain length up to 12 carbon atoms (Shapiro and Neal, *U.S. 2,992,251*). Hydrazides of acetic acid, sebacic acid, lauric acid, myristic acid or stearic acid were used as stabilizers for the alkali metal soaps of 12 to 18 carbon chain aliphatic monocarboxylic acids (Harshman and Fusco, *U.S. 2,963,438*). To stabilize a halogenated rubbery copolymer aqueous slurry agglomeration, scorching and pre-vulcanization,

there was incorporated 0.01-10% of an alkaline earth metal salt of a 5-30 carbon monocarboxylic fatty acid (Eby et al., *U.S. 2,958,667*). Water soluble salts of fatty acids of approximately these same chain lengths and carboxymethyl cellulose salts, mixed in proportions between 15:1 and 5:3, form an anti-tack composition (Kern et al., *U.S. 3,002,840*). Aluminum stearate mixed with lecithin was incorporated into an edible oil to form a pan dressing (Brody and Fahlen, *U.S. 2,963,372*). Water-insoluble fatty acid salts of multi-valent metals were formed by saponifying high molecular weight fatty acids with 2-10% excess of alkali carbonate and reacting this mixture with an acidified aqueous multi-valent metal salt solution (Meyer, *U.S. 2,993,921*).

Epoxidation and factors affecting the process were reviewed (Kovaes, *Fette, Seifen, Anstrichmittel*, 63, 251). Synthesis of hydroxy-amino fatty acids from epoxy compounds was summarized (Kaufmann et al., *Fette, Seifen, Anstrichmittel*, 63, 239). Ion exchange resins as catalysts for epoxidation, esterification, hydrolysis, and alcoholysis were reviewed (Ollero and Soto, *Grasas y Aceites*, 11, 29). An organic polyhydroxy compound containing 3-10 carbon atoms was used to improve epoxidation with hydrogen peroxide in the presence of an acid activator (Dieckelmann, *U.S. 2,992,237*). Complex epoxy fatty esters were prepared by mixing together two different esters, one of which was epoxidized, and heating at temperatures of 50-130°C in the presence of an alkaline esterification catalyst (Kuester and Findley, *U.S. 2,978,463*). A polybasic phosphorus acid was reacted with an epoxidized fatty oil having acyl radicals of 10-22 carbons and an epoxy content above about 2% oxirane (Findley, *U.S. 2,965,657*). A procedure for determination of olefinic bonds involved transformation of the olefin to the glycol monoacetate by treatment with 40% commercial peracetic acid, reaction of this with hydroxylamine and measurement of the hydroxamic acids as their wine-red ferric salts. Rearrangement of the epoxides with boron trifluoride and conversion of the resulting carbonyl compounds to solid dinitrophenylhydrazones was also suggested (Sharefkin and Shwerz, *Anal. Chem.*, 33, 635). As a corollary of this procedure, acetylenes were differentiated from olefins by hydrating the acetylenes using BF₃-mercuric oxide-trichloroacetic acid catalyst mixture, and converting the resulting carbonyl compounds to 2,4-dinitrophenylhydrazones (Sharefkin and Boghosian, *Anal. Chem.*, 33, 640).

Epoxidized sperm blubber oil was investigated as a stabilizer for vinyl chloride resins (Tateishi et al., *Kogyo Kagaku Zasshi*, 64, 1028). Epoxidation of the maleinized esters of sperm oil fatty acids and crude erucic acid was found to improve their properties as plasticizers for polyvinylchloride, although only low oxirane contents were obtained (Komori et al., *Yukagaku*, 10, 18). Epoxides and esters of maleic and acrylic acid adducts of safflower, soybean, and linseed esters and conjugated linoleic ester were evaluated as plasticizers for polyvinylchloride, polyvinylidene chloride and acrylonitrile rubber. In general, these adducts performed like petroleum type plasticizers, but were less volatile and less extractable (Teeter et al., *JAOCs*, 38, 117). In a study of the preparation of maleic ester adducts, yields of 80-90% were obtained from the reaction of dimethyl maleate with safflower oil, soybean oil or linseed oil at elevated pressures in the presence of SO₂ catalyst and hydroquinone inhibitor. Poorer yields were obtained with di-n-butyl maleate and both anthraquinone and a nickel conjugation catalyst. Linolenates were found to be most reactive, and under these conditions, oleate reacted very little (Miller et al., *JAOCs*, 38, 235). Methods of preparation and uses of hydroxylated and epoxidized fats and their derivatives were reviewed (Naudet, *Rev. Franc. Corp. Spec. No. April 28, 1960*, 7). Use of castor-oil-derived polyols in urethane foams was studied with respect to the effect of catalyst, silicone surfactant, and trichlorofluoromethane content (Lyon et al., *JAOCs*, 38, 262). Morpholides of selectively hydrogenated cottonseed acids and of epoxidized cottonseed acids were found to be good primary plasticizers for vinyl chloride homopolymer and copolymer resins, accept plasticizers for cellulose triacetate and possible softeners for Buna A (Magne et al., *JAOCs*, 38, 291). The effect of fatty acid composition on compatibility of the morpholides with vinyl-chloride-vinyl acetate copolymer systems was investigated (Magne et al., *JAOCs*, 38, 294). Divinyl sulfone adducts of methyl- α -eleostearate, its hydrogenated derivative, and the adduct to tung oil were found to be satisfactory plasticizers for nitrile rubber (Plaek et al., *JAOCs*, 38, 107). Differences in the reactivity of the terminal and branched carboxyl groups of carboxystearic acid, prepared by carbonylation of oleic acid with carbon monoxide, were utilized in preparing monoesters for evaluation as plasticizers. These monoesters were found to be incompatible with PVC, but the diesters through dipropyl, and carbomethoxyoctadecylacetate, were found to be efficient low tem-

perature plasticizers. Di-n-butyl carboxystearate was found to have a high viscosity index (169) and a low pour point (-54°C) (Roe et al., *JAACS*, 38, 527). Methods were developed for determination of alkoxy groups in polymers and copolymers containing alkyl acrylates and maleates (Miller et al., *Anal. Chem.*, 33, 677). A review discussed the relation of fats and oils to synthetic resins (Shigeno, *Yukagaku*, 10, 193).

Naturally occurring epoxy acids were detected and measured by paper, thin-layer, and gas-liquid chromatography. The last two methods proved to be particularly effective (Morris et al., *J. Lipid Research*, 2, 68). In another study, the epoxy acids were estimated by measurement of increased absorption at $2.795\ \mu\text{m}$ in the near infrared caused by chlorohydrins produced from the epoxides by treatment with anhydrous ethereal hydrogen chlorides (Morris and Holman, *J. Lipid Research*, 2, 77).

A mixture of nitric and sulfuric acids was used in the oxidative degradation of unsaturated fats. Azelaic, suberic and pelargonic acids were prepared from oleic; sebacic acid and isooctyl alcohol from ricinoleic acid; and *omega*-amino-undecanoic and pelargonic acids were prepared from oleyl nitrile (Pasero, *Rev. Franc. Corp. Gras. Spec. No.* April 28, 1960, 24). The effects of solvents on the ozonolysis of unsaturated acids were investigated using acetic acid, petroleum ether, cyclohexane, and chloroform. Effects of oxygen and hydrogen peroxide on oxidative cleavage of ozonides in chloroform were studied as a function of substrate concentration and temperature. It was shown that yields of dibasic acids are affected by impurities in starting materials and by the method of separation of the acids (Pasero and Naudet, *Fette, Seifen, Anstrichmittel*, 62, 190). A polyaldehydic oil which condensed with phenolic compounds, urea, amines, and polyols to give crosslinked polymers was prepared by ozonization of soybean oil followed by reductive decomposition of the ozonides (Pryde et al., *JAACS*, 38, 375). It was suggested that because of the high viscosity of the ozonides, ozonolysis of oleic acid should be carried out in the presence of solvent. The high percentage of polyunsaturated fatty acids in commercial oleic acid was also shown to increase ester formation by molecular rearrangement during ozonolysis, thus contributing to heterogeneity of the reaction product (Naudet and Pasero, *Fette, Seifen, Anstrichmittel*, 62, 1110). Unsaturated fatty acids were decarboxylated by treatment with sodium hydroxide at $200\text{--}500^{\circ}\text{C}$, forming methane, hydrogen and sodium carbonate as by-products (Takeshita, *Kogyo Kagaku Zasshi*, 63, 2159). A polymer formed by the reaction of a carboxylic acid group of a fatty acid mole with a double bond of fatty acid mole was obtained when fatty acids rich in oleic and linoleic acid were heated at 110 to 240 , with catalytic amounts of zinc chloride or zinc bromide admixed with a catalytic quantity of an acid catalyst such as HCl or HBr (Hampton, *U. S. 2,978,468*). Tensile strength and low temperature characteristics of copolymers of acrylonitrile with butyl, octyl or octadecyl acrylate were found to vary inversely with the wt % of the acrylate present without regard to its alkyl type. Long chain acrylates imparted slightly greater chemical resistance to the copolymers (Jordan et al., *JAACS*, 38, 231).

In a study of the effect of several variables on the hydrogenation of cottonseed oil, it was found that the over-all rate of hydrogenation was directly proportional to the degree of unsaturation and to the amount of nickel catalyst. The rate increased with increased pressure and temperature. Selectivity and isomerization decreased with pressure, but were little affected by temperature and the catalyst concentration (Wisniak and Albright, *Ind. Eng. Chem.*, 53, 375). Gas-liquid partition chromatographic data and the ultraviolet absorption of oil before and after hydrogenation were compared (Kaufman et al., *JAACS*, 38, 495). A positive relation was demonstrated between *trans*-isomer content of a hydrogenated oil and its congeal point. In both cottonseed and soybean oil, equilibrium was reached and saturation of *trans* isomers began to occur at an I. V. of $60\text{--}70$ (Stingley and Wrobel, *JAACS*, 38, 201). In catalytic hydrogenation of oiticica oil it was found that the use of zinc and chromium oxides as catalysts results in reduction of the keto and ester groups, but not the double bonds, to produce diene hydrocarbons (Kaufmann and Sud, *Fette, Seifen, Anstrichmittel*, 63, 138). X-ray diffraction examination of some standard catalysts showed their composition to be CuO and CuCr_2O_4 combined with Mn oxide, and $\text{Cu Cr}_2\text{O}_4$ combined with Mn oxide. The latter combination showed higher activity and selectivity on the unsaturated bonds of fatty oils (Takumi, *Yukagaku*, 10, 41). A similar study of Cu-Cr-Mn oxide catalyst, which had been used in the hydrogenation of unsaturated fatty oils, showed that the cupric oxide was largely reduced to metallic copper; but the cupric chromite combined with Mn oxide,

considered to be the true catalyst, was not reduced to cuprous chromite (Tokumi and Hashimoto, *Yukagaku*, 10, 150). Hydrogenation of methyl linoleate with hydrazine hydrate was investigated, separating the reaction products by countercurrent fractionation of the mercury adducts (Schilling, *Fette, Seifen, Anstrichmittel*, 63, 421). Countercurrent distribution analysis of the products of hydrazine reduction of linolenic acid to an acid value of 162 showed the reaction mixture contained 26% triene, 43% diene, 26% monoene, and 5% stearate. The procedure did not isomerize or shift the double bonds, although it appeared that double bonds farthest from the carboxyl were reduced at a slightly faster rate (Scholfield et al., *JAACS*, 38, 208). In a study of iodine and light catalyzed isomerization of conjugated trienes, the center double bond of the conjugated system isomerized less readily than the outer double bonds (Tolberg et al., *JAACS*, 38, 102).

Amides were formed in yields of 90% or better by aminolysis of methyl stearate at 30°C under anhydrous conditions in the presence of sodium methoxide catalyst (Jordan and Port, *JAACS*, 38, 600). Freezing point data were obtained for stable, metastable and the unstable crystalline phases in binary mixtures of the 1:1 molecular compounds, acetamide-palmitic acid and acetamide-stearic acid, and for a portion of the ternary system acetamide-palmitic acid-stearic acid (Mod et al., *J. Phys. Chem.*, 11, 1613). A polyamide of relatively high amine number was formed by reacting a copolymer of a conjugated alicyclic diene monomer and an alkali refined polyunsaturated glyceride with an alkylene polyamine having at least 3 amino nitrogens and at least 4 carbons (Hovey, *U. S. 3,001,960*). A procedure was described for spectrophotometric determination of fatty acid amides in lipids (Haskins, *Anal. Chem.*, 33, 1445). To eliminate end point difficulties and high apparent I. V. in the determination of unsaturation in high molecular weight fatty nitrogen compounds, primary and secondary amines were acetylated, acetic acid was used as solvent for tertiary amines, and sodium lauryl sulfate was added before titration of quaternary derivatives (Milun, *Anal. Chem.*, 33, 123). Reactions of tetra-cyclic ketene dimer with amines were investigated (Imai and Wakabayashi, *Yukagaku*, 10, 165). Acyl taurides were produced by reaction of a higher molecular weight fatty acid anhydride with one mole of a taurine salt in aqueous solution (Lorentzen, *U. S. 2,967,872*). Procedures were described for synthesis of N-methylcephalins (Baer and Pavanaram, *J. Biol. Chem.*, 236, 1269), N,N-dimethylcephalins (Baer and Pavanaram, *J. Biol. Chem.*, 236, 2410) and distearyl-L- α -glycerylphosphoryl-L₂,L₃-hydroxyproline (Baer and Zschocke, *J. Biol. Chem.*, 236, 1273). Melting points of urethanes prepared from highly purified fatty alcohols and fatty isocyanates, wherein chain lengths were varied from $8\text{--}22\text{C}$ atoms, were found to be dependent upon the total number of carbon atoms and the symmetry of the molecule (Shulman et al., *JAACS*, 38, 205).

Esters of monohydric alcohols and tall oil fatty acids showed improvement in color processing modifications such as fast cooling by addition of cold water to the ester solution, vacuum topping before water washing, and use of carbon dioxide as a blanketing gas (Bauer et al., *JAACS*, 38, 127). Methods investigated for methyl-esterification of tall oil included heating the oil and methanol with or without catalysts in an autoclave, and reacting the soap of the oil with methyl iodide or dimethyl sulfate. Zinc chloride, magnesium oxide and active clay were effective as catalysts for the reaction with methanol (Nakasato, *Yukagaku*, 10, 37). Urea adduct separation of mixtures of fatty acids, esters, and waxes was reviewed (Srivastava, *Indian Oil & Soap*, 3, 51). Yields of methyl linoleate isolated from safflower oil esters by the urea adduct method were increased 13.9% by concentrating the mother liquor from the fourth crystallization and adding urea (Johnson and Ali, *JAACS*, 38, 453). In gas chromatography of methyl esters of fatty acids and their autoxidation products, high temperature plus metal catalysis by components of the flash heater were found to promote alterations involving dehydration and deacylation of oxidation products (Morris et al., *J. Lipid Research*, 1, 412). Four methods for preparation of methyl esters of fatty acids for gas chromatography were compared quantitatively (Vorbeck et al., *Anal. Chem.*, 33, 1512). Fatty acid esters for gas chromatographic analysis were prepared rapidly and quantitatively by boiling the fatty acids in an excess of boron trifluoride-methanol reagent for as little as 2 minutes (Metcalf and Schmitz, *Anal. Chem.*, 33, 363). Effects of the column support on separation of fatty acid methyl esters by gas chromatography were reported (Hornstein and Crowe, *Anal. Chem.*, 33, 310). Two numerical constants, one obtained by use of polar packing, the other by use of non-polar packing, were reported to adequately characterize mono- and dicarboxylic acids in gas-liquid chromatography (Mirva et al., *Anal. Chem.*,

13, 1739). For gas-liquid chromatographic separation of methyl esters of fatty acids, waxes, sterols and tocopherols, silicone rubber gums, and grease were used as the stationary phase at low concentration and high temperature (Nicolaidis, *J. Chromatography*, 4, 496).

Glycidyl esters of various commercial and pure fatty acids were prepared by reaction of the salts of the carboxylic acids with epichlorohydrin in the presence of quaternary ammonium halides (Maerker et al., *JAACS*, 38, 194). In a similar patented process, 9 to 13 moles of epichlorohydrin per mole of fatty acid was added to a mixture of molten fatty acid, alkali metal carbonate and quaternary ammonium halide catalyst (Nevin and Fletcher, *U.S. 2,992,239*). The 16-32 carbon symmetrical- α -glycols were prepared from acyloins by catalytic hydrogenation with Raney nickel (Fukushima and Shimokai, *Yukagaku*, 10, 6). α and β methylene glycerol esters of fatty acids were prepared by heating methylene glycerol isomers in the presence of fatty acid esters and litharge. These products were reacted with benzene in the presence of aluminum chloride to obtain 75% yields of monoglycerides consisting of 88% α and 12% β monoglycerides. Isopropylidene glycerol esters failed to react (Blazot and Richert, *Oleagineaux*, 15, 851). 1- and 2-Monoglycerides were differentiated and mixtures analyzed by measurement of the overtone of the OH stretching vibration appearing at 1.4 μ in the near infrared spectral region (Susi et al., *JAACS*, 38, 199). Acetylated mono- or diglycerides, or mixtures, were patented as coatings for meat products to prevent sticking of the casings (Brissey and Hill, *U.S. 2,982,660*).

Patents described preparation of partial fatty esters of inositol using as solvent dimethylacetamide (Huber and Martin, *U.S. 2,997,491*), and dimethylsulfoxide (Huber, *U.S. 2,997,490*). A sulfoxide or an amide solvent was also used in a process for preparing straight chain hexitol fatty esters by interesterification (Huber, *U.S. 2,997,493*). Still another patent substituted pyridine for these solvents (Martin, *U.S. 2,997,492*). Water soluble carboxylic acid monoesters of carbohydrates were patented as new compounds (Gaertner, *U.S. 2,973,353*). Finely divided sucrose was reacted with a lower alkyl ester of a higher fatty acid in the presence of a finely divided basic compound in a liquid hydrocarbon medium to form sucrose monoesters (Curtis, *U.S. 2,999,358*). Vinyl esters were prepared by reaction of fatty acids with acetaldehyde, by interesterification of fatty acids with vinyl esters, and by direct vinylation of fatty acids with acetylene. Vinyl ethers were prepared by transesterification and by direct vinylation of fatty alcohols. Polymers and copolymers of both types of compounds were prepared and evaluated (Uzzan, *Rev. Franc. Corps Gras*, *Spec. No. April 28, 1960*, 13). Vinyl esters of a saturated fatty acid were separated from excess fatty acid by cooling to 2-10°C above the melting point of the vinyl ester, filtering off the precipitated fatty acid and molecularly distilling the filtrate to recover the vinyl ester in high purity (Kuhn and Wilip, *U.S. 2,957,015*). A water-soluble polyethylene glycol ester of a phytosteryl acid ester of a dicarboxylic acid was claimed in a patent (Stern, *U.S. 3,004,943*). Limited chemical and physical data suggested Tung Toxin I and Tung Toxin II from tung kernel meal are diesters of a 2,3-unsaturated-5-keto acid, a polyhydroxy acid and a 3,4-unsaturated-5-keto tertiary alcohol (Holmes and O'Connor, *JAACS*, 38, 520).

Unsymmetrical acetals were prepared from stearyl, oleyl, and mixed alcohols derived from linseed oil by acid catalyzed addition of each alcohol to ethyl vinyl ether. Cleavage of ethanol from these products yielded the corresponding alkyl vinyl ethers. Yields were moderate for the higher alkyl vinyl ethers because of disproportionation and formation of ethyl vinyl ether (DeJarlais et al., *JAACS*, 38, 241). Temperature coefficients of the dielectric constants of aliphatic alcohols were found to be directly proportional to the carbon chain length of the aliphatic group (Oehme, *Fette, Seifen, Anstrichmittel*, 62, 910). It was found that fine dispersions of carbon, when coated with a monolayer of fatty alcohol or fatty acid which coordinates with detergents, remained as stable dispersions in the presence of calcium ions (Peper and Rosanov, *JAACS*, 38, 500). A new procedure for the preparation of the esters of tertiary alcohols consists of quantitative alcoholysis of fatty acid esters of primary or secondary alcohols with tertiary alcohols in the presence of alkali-tertiary alcoholates as catalysts (Balter and Wechmann, *Fette, Seifen, Anstrichmittel*, 63, 601). Reviews of alcohols included a review of the synthesis of higher alcohols (Murahashi, *Yukagaku*, 10, 383) and a review of the sperm alcohol industry (Kashima, *Yukagaku*, 10, 387).

Liquid 18 carbon saturated monocarboxylic acids were obtained in yields exceeding 30% by treating linseed oil in ethylene glycol with excess sodium hydroxide at 295°C, fractionally distilling, hydrogenating and removing straight chain compounds by fractional crystallization (Friedrich et al.,

JAACS, 38, 329). Ultraviolet and infrared studies of the thermal isomerization of methyl linoleate isomers showed that conjugated isomers tend to go to the *trans-trans* form which then slowly isomerizes to *trans-trans* non-conjugated. The resulting *trans-trans* non-conjugated form does not change to other isomers, but slowly dimerizes to the extent of about 25% (Nagano and Tanaka, *Yukagaku*, 10, 146). Alkali isomerization of non-conjugated into conjugated fatty acids was studied (Balter et al., *Fette, Seifen, Anstrichmittel*, 63, 413). Oxygen was reported to increase the rate of isomerization of *cis*-methyl linoleate to *trans-trans* conjugated or *trans* non-conjugated forms even at room temperature (Nagano and Tanaka, *Yukagaku*, 10, 29). The 8,12-linoleic acid formed during hydrogenation of oils containing linoleic was separated from the 9,12-isomer by paper chromatography of the rhodan derivatives (Moller and Gabrielsson, *Fette, Seifen, Anstrichmittel*, 62, 936). *Trans*-10-hydroxy-2-decenoic acid, the acid present in royal jelly from queen bees, was synthesized from ricinoleic acid (Fujii et al., *Nippon Kagaku Zasshi*, 81, 1782). Methyl oleate was brominated in the allyl position using N-bromosuccinimide, and the influence of reaction kinetics, the concentration of oleate, and the molar ratio of N-bromosuccinimide to ester on yields of brominated products were studied (Naudet and Ucciani, *Fette, Seifen, Anstrichmittel*, 62, 691). Additional evidence was presented for the occurrence together of the cyclo-propenoid acids, sterculic acid and malvalic acid (Wilson et al., *JAACS*, 38, 696). The amount of hydroxyl forming hydrogen bonding in mixed crystals of 10-hydroxystearic acid and stearic acid was found to be proportional to the square of the hydroxystearic acid content (Nakajima and Toyama, *Nippon Kagaku Zasshi*, 81, 1472). The reaction of tetradecyl ketene dimer with hydroxyl radicals in the presence of catalysts was studied (Imai et al., *Yukagaku*, 10, 49). A thixotropic gel was formed by aging the product of the reaction of an unsaturated long chain aliphatic monocarboxylic acid glyceride, or an oil-modified alkyd resin, with arylene diisocyanate in the presence of particles of a hydrated siliceous material (Ferrigno, *U.S. 2,975,071*). Preparation of Diels-Alder adducts of a wide range of materials was described (Kaufmann et al., *Fette, Seifen, Anstrichmittel*, 63, 633). Chromatostrips were found to give rapid and convenient analysis of fatty acid derivatives using either ascending or descending chromatography (Applewhite et al., *JAACS*, 38, 609). Gel formation during dehydration of fatty mixtures was prevented by adding a fat liquid medium to obtain a ratio of total fat to non-fat solids of about 2 while increasing the concentration of discrete non-fat solids in the continuous fluid system (Greenfield, *U.S. 2,979,408*). A proposal for a new oral system for designating long chain fatty acids included numerical designation of the chain length followed by a numerical designation of the position of the first double bond in a serialized unsaturated system (Morris, *JAACS*, 38, 197). Products produced from sunflower seed were listed (Mizuno and Guerrero, *Rev. Arg. Grasas y Aceites*, 3, 39). Research on the utilization of soybean oil was reviewed (Cowan, *JAACS*, 38, 12).

FATTY MATERIALS USED IN TEXTILE AND PAPER TREATMENT, WATER-PROOFERS, CORROSION INHIBITORS, WAXES, DEFOAMERS, WELL-DRILLING FLUIDS, INCENDIARY PREPARATIONS, AGRICULTURAL AND MISCELLANEOUS

Alkylsucroses prepared by reacting sodium succrate with higher alkyl bromides in dimethylsulfoxide are believed to be the first sugar-based surfactants which are at least equivalent to the best anionics and non-ionics in cloth detergency (Gaertner, *JAACS*, 38, 410). A composition for fat-liquoring leather included a cationic amine salt and a condensate of a fatty acid, glyceride or ester with a dialkanolamine (Retzsch et al., *U.S. 2,974,000*). A mixture of abietic acid and fatty acids of 8 to 22 carbons, dispersed in water by the wetting action of ammonium soaps, was described as a water-repellent composition for textiles (Lawler and Ballou, *U.S. 2,997,407*). An aqueous sizing for glass fibers contained 1-10% of a Werner complex in combination with from 3-10% of a partially dextrinized starch, 3-10% of a hydrogenated vegetable oil lubricant, 0.1-10% of an emulsifying agent, 0.4-4% of a fatty acid cationic amine softening agent, 0.03-2% gelatine and 0.05-1% polyvinyl alcohol (Gagnon and Rammel, *U.S. 2,993,872*).

An anti-sludging hydrocarbon fuel oil was prepared by treating the oil with 0.0001% to 0.1% by wt of a sucrose mono- or diester in which the sucrose is esterified with an aliphatic carboxylic acid having at least 8 carbon atoms (Ownby and Davis, *U.S. 2,992,082*). Rust preventive oils were reviewed (Kashima, *Yukagaku*, 10, 110). The stearyl

amine salt of maleinated oleic acid was found to be a better rust preventive than the product obtained by partially reacting the maleinated oleic with compounds containing OH, NH₂ or NH and then neutralizing with stearyl amine. Exceptionally good results were obtained with the amine salt of the derivative of N-octadecyl glycine (Sato et al., *Kogyo Kagaku Zasshi*, 64, 1017). Among organic thickening agents proposed for use in a mono-propellant composition comprising a dispersion of ammonium nitrate suspended in the thickening agent and dissolved in a non-explosive solvent were fatty oils, waxes, fats, long chain fatty acids or their cellulose esters, natural resins and gums, and synthetic resins or pitches (Taylor and Budd, *U. S. 2,966,404*).

Data were presented indicating peat wax contains aliphatic, 19-22 carbon, monocarboxylic acids and aliphatic, 20-21 carbon, monohydroxy acids (Rauhala, *JAACS*, 38, 233). Physical and chemical properties of a previously unreported cuticle wax from the Cuban palm showed the wax to be quite similar to carnauba (Kitzke and Wilder, *JAACS*, 38, 699). The n-paraffin and primary alcohol fractions of plant waxes were re-examined by mass spectroscopy and both odd and even number members were shown to be present. Iso-Paraffins were found in rose petal wax and in tobacco-leaf wax, but in no other wax examined (Waldron et al., *Biochem. J.*, 78, 435). A procedure for chromatographic separation of even numbered wax acids up to 36 carbon atoms was described (Kaufmann and Das, *Fette, Seifen, Anstrichmittel*, 63, 614). Waxy constituents were separated from the sterols of tall oil or crude cane oil by dissolving in ethylene dichloride, removing the water and cooling to precipitate the wax (Miller et al., *U. S. 3,004,992*). Hard waxes were produced by esterification of an aliphatic carboxylic acid containing more than 18 carbon atoms with an aromatic dimethylol compound, a mixture of aromatic dimethylol and methylol compounds, or mixtures of these with dihydric to tetrahydric aliphatic alcohols (Kaüpp, von Rosenberg and Träger, *U. S. 2,963,379*). Waxes were bleached with chromosulfuric acid at 90°C or above, and mixed with a solid, oxidized aliphatic hydrocarbon to form a new composition of matter (Zinnert, *U. S. 3,004,856*). Polyoxyethylene derivatives of the sorbitan esters of 12 to 18 carbon fatty acids and the sorbitan esters of these fatty acids were used together as surface active agents in forming a fluid, high solids, emulsified wax composition for coating candles (Rockland, *U. S. 3,000,753*). Glyceride wax was patented as a coating for citric acid powdered to at least as fine as 30 mesh (Grief, *U. S. 2,956,926*).

A soapstock to be added in small amounts to glyceride oil meal in feed compositions was prepared from a glyceride oil containing free fatty acids and gums by adding sufficient soda ash to precipitate the gums and react with at least some of the free fatty acids (Thurman, *U. S. 2,963,559*). The AOAC method gave erroneous results for the crude fat of expanded dog food, and a replacement procedure was recommended (Hoffman, *J. Assoc. Offic. Agr. Chemists*, 44, 556). As synergists in a fly repellent composition, oleic acid, sorbitan trioleate, sorbitan monooleate, linoleic acid, ricinoleic acid, propyl oleate or benzyl oleate were used (Bruce, *U. S. 2,991,219*). Cabbage leaf phospholipids were found to contain predominantly palmitic, linoleic and linolenic acids. Phosphatidyl glycerol and an unknown glycerophospholipid were also separated (Wheeldon, *J. Lipid Research*, 1, 439). Waste liquor from olive oil extraction was suggested as a possible fertilizer (Albi and Piestas Ros, *Grasas y Aceites*, 11, 123). Paper chromatography of "oleuropeina", a bitter glucoside in olives, evidenced a mixture of three substances (Vasquez et al., *Grasas y Aceites*, 12, 19). Determination of the hydroxyl numbers of the unsaponifiables of olive oil was found to be a good method for characterizing this fraction (Gracian and Martel, *Grasas y Aceites*, 11, 59).

FATTY MATERIALS IN LUBRICATION, METAL-WORKING AND TEXTILE OILING

An oil-compatible fatty acid amide of phenothiazine was added to a lubricant composition to impart improved oxidation stability at temperatures of 300 to 450°F. (Nelson, *U. S. 2,998,386*). Aluminum tristearate, aluminum naphthenate and the aluminum soap of a branched chain, 8 carbon, saturated fatty acid were added in specified ratios to each other to a lubricating oil to thicken the oil (Franklin and Gebhart, *U. S. 2,998,385*). A shear-stable and substantially water-insoluble lubricating grease composition included the lithium soap of a high molecular weight fatty acid and lithium dilinoleate as thickening agents (Eckert and Thomas, *U. S. 2,983,680*). A high molecular weight fatty acid containing hydroxyethane groups, produced by hydrogenating the epoxidized fatty acid, was added as a soap to a liquid lubricating

oil to cause thickening (Clarke and Eckert, *U. S. 3,000,823*). A lubricating oil composition comprised the reaction product obtained by heating together at 400-700°F, 2-75 molar proportions of a one to 6 carbon fatty acid, 0.05 to 5 molar proportions of a 6-30 carbon fatty acid, one molar proportion of a cyclic hexanone and an alkali or alkaline earth metal base dispersed in the oil (Morway and Bartlett, *U. S. 2,962,441*). Air-free aluminum stearate grease was produced by cooling the hot composition under reduced pressure (Richards and Thompson, *U. S. 2,962,440*). Reviews discussed the problems of wetting to metallic surfaces and oil (Goto, *Yukagaku*, 10, 71), and the spreading of lubricating oil on metallic surfaces (Takahashi, *Yukagaku*, 10, 99).

Good pickling inhibitors for soft steel were formed by adding 15 moles of ethylene oxide to soybean oil fatty amides (Babu and Bushita, *Kogyo Kagaku Zasshi*, 63, 1138). A cutting oil composition included anhydrous mineral oil, benzyl polysulfate and about 5% of calcium stearate (Stine and Hughes, *U. S. 2,995,516*). Reviews summarized metal cutting oils (Mugishima, *Yukagaku*, 10, 76); friction in cutting of metals (Shonoaki, *Yukagaku*, 10, 71); quenching oils (Mito, *Yukagaku*, 10, 104); rolling oils for non-ferrous metals (Shimizu, *Yukagaku*, 10, 88); rolling oils for steel plates (Saeki, *Yukagaku*, 10, 83); and the washing of metals (Koike, *Yukagaku*, 10, 93). A drawing lubricant for application to metal from admixture with water included 15-45% by wt of a fatty acid soap, a metal borate and from 0.75 to 2.0% by wt of solids of a polyethylene glycol having a mol wt of at least 1000 (Brown, *U. S. 2,958,659*).

PRODUCTS (EXCEPTING DETERGENTS)

DRYING OILS, PAINTS, RESINS AND PLASTICIZERS

RAW MATERIALS AND PROCESSES. A review covered the use of fats and oils in synthetic resins (Shigeno, *Yukagaku*, 10, 193). A summary of twenty years of oil research at the Northern Regional Research Laboratory discussed the preparation of polymeric fatty acids and their use in resins, the production of conjugated unsaturation in oils, the polymerization of fatty vinyl ethers, and the preparation of aldehyde-acids by ozonization of fatty esters. The aldehyde-acids were converted to polymeric materials by acetal formation and esterification with polyhydric alcohols (Cowan, *JAACS*, 38, no. 5, supp. 12). Many problems facing the future of the paint industry such as education and training, information handling, communications, and creativity were discussed (Heiberger, *Offic. Dig., Federation Soc. Paint Technol.*, 33, 1566).

A paper on the production of linolenic acid from linseed oil enumerated the following potential uses for the acid and its derivatives: polymeric acids in polyurethane coatings, resins, and foams, polymeric acids in asphalt compositions for roads, polymeric acids in polyamide coatings to restrict the burning of solid rocket propellents, linolenyl vinyl ether coatings, epoxidized linolenate esters as plasticizer-stabilizers in vinyl resins, and linolenate esters as antiozonant-plasticizers in rubber products (Beal et al., *JAACS*, 38, 524). Changes, such as in fatty acid composition, of safflower seed and linseed oils during growth of the plants were studied (Sims et al., *Ibid.*, 273). A review covered the various products produced from sunflower seed (Mizuno and Guerrero, *Rev. Arg. Grasas y Aceites*, 3, 39). The fatty acid composition of herring oil was studied by gas chromatography (Klenk and Briker-Voigt, *A. Physiol. Chem.*, 324, 1). The fatty acid compositions of the seed oils of *Asphodelus fistulosus* (*piazi*), (Khan et al., *JAACS*, 38, 452) and "White Todri" (*Matthiola incana*) (Rahman and Khan, *Ibid.*, 281) were determined. These oils had I.V. of 142 and 139 respectively. Examination of seed oils from 37 plant species in the family Cruciferae revealed several with I.V. in the drying oil range (Mikolajczak et al., *Ibid.*, 678). The usefulness of Isano oil in intumescent fire retardant coatings and as a raw material in varnish and resin design was discussed (Cummings, *Offic. Dig., Federation Soc. Paint Technol.*, 33, 408). A procedure for control of alcoholysis and acidolysis of triglyceride oils was described (Meke and Staddon, *J. Oil and Colour Chemists' Assoc.*, 44, 497).

A review covered recent problems in the oxidation of oils (Shimamura, *Yukagaku*, 10, 129). A kinetic study of the cobalt stearate-catalyzed oxidation of linoleic acid supported the hypothesis that trace metal catalysis and the initiation of autoxidation were closely connected (Heaton and Uri, *J. Lipid Research*, 2, 152). Many aspects of the problem of the air-oxidation of rosin, abietic acid, and resinates were reviewed (Norwitz, *Offic. Dig., Federation Soc. Paint Technol.*, 33, 548).

Ozonization of soybean oil, followed by reductive decomposition of the ozonides, produced polyaldehyde oils. Reaction of these oils with phenols, urea, amines, and polyols gave cross-linked polymers (Pryde et al., *JAACS*, 38, 375).

Unsaturated fatty acids were polymerized by heating at 110–240F with an acid catalyst and a zinc chloride or bromide catalyst. Condensation of a carboxylic acid group of one molecule with a double bond of another was one of the reactions involved (Hampton, *U. S. 2,978,468*).

A complete theoretical discussion of alkali isomerization was followed by examples of the isomerization of linoleate and linolenate esters (Balter et al., *Fette, Seifen, Anstrichmittel*, 93, 413). Thermal isomerization studies at temperatures up to 200F in the presence of air and nitrogen containing lower amounts of oxygen were carried out on cottonseed oil, methyl oleate, and especially on four geometric isomers of methyl linoleate (*cis* and *trans* non-conjugated, and *cis-trans* and *trans-trans* conjugated). End products were the *trans-trans* conjugated and *trans* non-conjugated isomers, the first of these isomerizing slowly to the second. Increasing the amount of oxygen increased only the rate of isomerization. At the higher temperatures, the total amount of *trans* isomers increased (Nagano and Tanaka, *Yukagaku*, 10, 29, 146; Fukuzumi, *Ibid.*, 143).

A variety of products have been prepared based on the esterification of fatty acids with polyols other than glycerol. A linoleum cement was prepared by oxidizing and gelling in an aliphatic hydrocarbon solvent at 160–240F, a partially esterified tall oil in which the fatty acid portion only had been esterified with a 3–5 carbon polyhydric alcohol (Forsythe, *U. S. 2,985,535*). A partial ester of pentaerythritol with fatty acids or benzoic acid was heated at 150–230 with an acid catalyst to cause esterification, producing the corresponding partially esterified dipentaerythritol (Kraft, *U. S. 2,985,601*). Alcoholysis of the ester of a drying oil fatty acid and a volatile lower alcohol with sucrose or raffinose produced fatty saccharide esters containing at least four fatty acid groups per molecule of saccharide (Hass, *U. S. 2,970,142*). The carbonyl groups in a copolymer of styrene and acrolein or their derivatives were reduced to hydroxyl. The resulting polymer was esterified with unsaturated fatty acids to give an air-drying product (Hahn, *U. S. 2,984,633*). A drying oil was produced by esterifying an oxyalkylated (with ethylene or propylene oxide) phenol-formaldehyde novolak with carboxylic acids, at least 60% of which were drying oil fatty acids (Partansky, *U. S. 2,967,838*). A coating composition was prepared by treating a solution of a soybean or tall ester of Bisphenol A (acid value 3.8–5.2) with an aluminum isopropylate-ethyl acetoacetate chelate. The resulting gel was agitated until dissolved (Heck, *U. S. 3,001,959*).

A discussion of the markets for tall oil pointed out that the major use for tall oil fatty acid is in the production of alkyd resins for protective coatings (Ruskin, *JAOCs*, 33, no. 3, supp. 33). Nyasaland and Chinese tung oils performed similarly when used with either linseed or soybean oil in alkyd resins (Chatfield, *Paint, Oil and Colour J.*, 32/33, 742). A procedure for preparing alkyd resins involved heating the polyhydric alcohol, the polybasic acid, and 20–90% of the monobasic acid component (4–22 carbon atoms) at 150–290 to an acid value below 20, then adding the remainder of the mono-basic acid and continuing the reaction at 190–300 to an acid value below 15 (Kraft, *U. S. 2,973,331*). Alkyd resins were prepared by acidolysis of a triglyceride oil with phthalic anhydride and a fatty acid, followed by addition of a polyhydric alcohol and esterification of the free carboxylic acid groups (Carlston, *U. S. 3,001,962*). Similar reactions were carried out using isophthalic and terephthalic acids for acidolysis of the triglyceride (Carlston, *U. S. 2,991,259*).

In addition to the usual polybasic acids and anhydrides used in alkyd resins, the following materials were used: trimellitic acid and anhydride, trimelic acid, hemimellitic acid and anhydride (Bolton and Van Strien, *U. S. 2,960,485*; *U. S. 2,985,603*), the water-soluble mixed aromatic acids produced by oxidation of coal (Rickert, *U. S. 2,965,587*), and a diene dibasic acid having 14–26 carbon atoms (Smith and May, *U. S. 2,957,837*). Aromatic monocarboxylic acids were used as ingredients of alkyd resins (Heinrich et al., *U. S. 2,993,873*). The specific acids included the following: 2,4-dichlorobenzoic, 2,4-dimethylbenzoic, p-bromobenzoic, 2,5-dihydroxybenzoic, p-hydroxyphenylacetic, 5-bromosalicylic, 3-hydroxy-2-naphthoic, p-phenylbenzoic, and m-bromobenzoic (Heinrich et al., *U. S. 2,979,472–4*; *U. S. 2,981,705–8*; *U. S. 2,982,747–8*).

Emulsified alkyd coating compositions were prepared from fatty acids or glycerides, dicarboxylic acids, and two different polyols, one monomeric and the other polymeric. Acid values were between 5 and 75. The emulsions were stable without the addition of protective colloids (Armitage and Trace, *U. S. 3,001,961*). Other alkyd emulsions contained, in the continuous aqueous phase, a water-soluble salt of an acidic alkyd resin and, in the dispersed phase, the in-situ polymerization product of a vinyl compound with an alkyd resin, the poly-

basic acid constituent of the latter alkyd being an α,β -ethylenic polycarboxylic acid (Boller, *U. S. 2,992,197*).

Fatty acids can be converted into polymers or polymerizable materials by other means than esterification with polyols. One such method is the formation of vinyl esters. Such esters were prepared by the reaction of fatty acids with acetaldehyde, with acetylene, and with vinyl esters of other acids. Polyvinyl stearate was used as a plasticizer. Co-polymerization of vinyl stearate with other monomers was studied (Uzzan, *Rev. Franc. Corp. Gras, Spec. No.*, April 28, 1960, 13). Vinyl esters of saturated fatty acids were freed of fatty acid by crystallization of the fatty acid, followed by molecular distillation of the ester (Kuhn and Wilip, *U. S. 2,957,015*). Copolymers of fatty vinyl esters with vinyl formate were rendered more water resistant by hydrolysis to remove the formate groups (Jordan et al., *U. S. 2,984,652*).

Fatty derivatives containing free hydroxy groups react with polyisocyanates to give polyurethanes. Such resins were prepared from hydroxyl-containing materials prepared as follows: by alcoholysis of a drying oil with an aliphatic alcohol (at least trifunctional) at 420–550F to give a diol ester (Hauge and Pawlak, *U. S. 2,970,062*), by alcoholysis of castor oil with a polyoxypropylene ether of a hexitol (Ruekin et al., *U. S. 2,994,674*), and by alcoholysis of castor oil with a glycol having 2–4 carbon atoms. The product of the reaction of the latter polyol with a diisocyanate was used as a drying oil after addition of castor oil and an N-substituted diethanol amine (Schwarzman, *U. S. 3,001,958*). The production of rigid foams from tolylene diisocyanate and the following castor derivatives was studied: castor oil, hydroxylated castor oil, glycerol, pentaerythritol, and sorbitol monoricinoleates, and N,N-bis(2-hydroxyethyl)ricinoleamide. Foams of greater strength and dimensional stability were obtained by mixing the castor polyols with a polyol of lower mol wt (Lyon et al., *JAOCs*, 33, 262). A mixture of a fatty triglyceride or an oil-modified alkyd resin with 0.5–5.0% of an aromatic diisocyanate containing particles of a hydrated siliceous material formed a thixotropic gel upon standing (Ferrigno, *U. S. 2,975,071*).

The introduction of epoxy groups into fatty acids and oils increases their functionality. (See the paragraph on plasticizers (below) for other information on epoxidized fatty derivatives.) Methods of preparation and reactions of epoxy compounds were reviewed (Kaufmann et al., *Fette, Seifen, Anstrichmittel*, 63, 239). The effects of processing variables on the epoxidation of unsaturated esters were studied (Kovacs, *Ibid.*, 251). Unsaturated fatty oils and other unsaturated compounds were epoxidized with aqueous hydrogen peroxide solution, in the presence of an acid activator capable of accelerating peracid formation, and an organic polyhydroxy compound (such as monosaccharides, sugar polysaccharides, amylose, amylopectin, dextrans, glycogens, and pectins) (Dickelmann, *U. S. 2,992,237*). The use of ion-exchange resins for catalyzing the epoxidation of fats was reviewed (Ollero and Soto, *Grasas y Aceites* 11, 29). The equilibrium constant in the formation of peracetic acid (often used in epoxidizing fats) from acetic acid and hydrogen peroxide was 3.26 in the range of 25–45. The activation energy was 11.7 kcal/mole with sulfuric acid as the catalyst (Murai et al., *Kogyo Kagaku Zasshi*, 63, 1233).

Interesterification reactions were carried out between two different esters, one of which was an ester of an epoxidized fatty acid (Kuester and Findley, *U. S. 2,978,463*). Polymers were prepared from epoxidized fatty esters and polycarboxylic anhydrides (Budde and Matson, *U. S. 2,993,920*), and from fatty polyepoxides, dibasic acid or dihydric alcohol, and 1,4-5,6,7,7-hexachlorobicyclo-(2,2,1)-5-heptene-2,3-dicarboxylic anhydride (Ilardo et al., *U. S. 2,992,196*).

Reaction of polymeric (polycarboxylic) fatty acids with polyamines produces polyamide resins. The copolymer of an alicyclic conjugated diene monomer with an unsaturated glyceride oil was used as the acid component in such a preparation (Hovey, *U. S. 3,001,960*). Heating polyamides with a variety of nitrogen-containing compounds above the decomposition temperature of the nitrogen compound produced resins of improved toughness and decreased tackiness (Young and Luce, *U. S. 2,992,195*). A thixotropic coating vehicle was prepared by reaction of a polyamide resin with a fatty ester (glyceride oil, oil-modified alkyd resin, or varnish ester). The course of the reaction was followed by observing the light transmission of a sample of the reaction mixture after dilution with a solvent in which the polyamide was insoluble and the reaction product was soluble (Toussaint and Anagnostou, *U. S. 2,962,461*). A review covered the production of thixotropic paint and varnish materials (Ivanov et al., *Lakokrassochnya Materialy i ikh Primeneie*, 4, 21–7). Thixotropic varnishes were prepared by heating diamines such as tetramethylene diamine

with oils and fatty acids, such as linseed oil and linseed oil fatty acids (Zankl and Hebermehl, *Ger. 1,096,519*). Such paints were also prepared by adding small amounts of N-alkyl-Y-hydroxy carboxylic acid amides to a drying oil composition (Grifo and Mayhew, *U. S. 2,872,332*), or by adding an organic polyisocyanate (Ferrigno, *U. S. 2,975,071*). A method was described for classifying and predicting the thixotropic behavior of plastic materials (DeWaele, *J. Oil and Colour Chemists' Assoc.*, 44, 377).

Reaction with other unsaturated compounds is a common means of upgrading fatty acids and oils. Reaction of maleate and fumarate esters with safflower, linseed and soybean oils under pressure in the presence of sulfur dioxide, anthraquinone or nickel catalysts was studied. The reaction occurred on linoleate and linolenate chains, the latter being more reactive. There was little reaction with oleate chains (Miller et al., *JAOCs*, 38, 235). Diels-Alder adducts were prepared from β -eleostearate esters with acrylic acid, crotonaldehyde, ethyl crotonate, and diethyl acetylene dicarboxylate and from methyl β -leanate with acrolein, acrylic acid, crotonaldehyde, ethyl crotonate, and methyl vinyl ketone (Kaufmann et al., *Fette, Seifen, Anstrichmittel*, 63, 633). A polyester resin formed from an unsaturated aliphatic dicarboxylic acid and a fatty monoglyceride was cross-linked with a vinyl monomer (Wet-roff and Raitzyn, *U. S. 2,983,695*). An alkyd resin was formed from molten phthalic anhydride, a polyhydric alcohol, and the polymerization products of styrene with a drying oil, fatty monoglyceride, or fatty acid (Hart, *U. S. 2,982,746*). A thixotropic vehicle was prepared by heating a drying oil, bodied drying oil, or a drying oil-vinyl (styrene or vinyl-toluene) copolymer at 200–450°F in the presence of 0.1–5% of ethylene diamine (Schroeder et al., *U. S. 2,996,396*). Synthetic drying oils were prepared by the copolymerization of cyclopentadiene with linseed and soybean oil and a compound containing one or more unconjugated double bonds (Gerhart, *Ger. 1,009,174*). Polymers resulting from unsaturated fatty acids and olefinic compounds were used as paint driers (Mikush and Mills, *Ger. 1,089,551*). Improved drying oils were obtained by heating linseed oil and castor oil under nitrogen in the presence of toluene sulfonic acid, cooking and further heating after adding adipic acid (Petzold, *Ger. [East]*, 20,443). Film formation of conjugated and nonconjugated drying oils, including the effect of catalysts, was reviewed (Dyck, *Farbe u Lack*, 67, 442).

Materials of complex composition have been prepared by combining a drying oil product with one or more resins of other types. These combinations may be made by simply mixing the various polymeric materials, causing them to react with one another, or mixing and then reacting the various monomeric materials which would ordinarily go into the preparation of the separate resins. An oil resistant material for coating gaskets was prepared from blown castor oil and a dimethyl silicone (Brownback, *U. S. 2,956,908*). A paint vehicle with fungicidal properties was prepared from a drying oil and/or drying oil acid, hexachlorocyclopentadiene, and a hydroxyl-containing film-forming resin (Goldblatt and Hopper, *U. S. 2,984,632*). A rapid drying coating material of good stability was prepared from a dehydrated castor alkyd and an amino urea resin (Gaynes, *U. S. 2,932,745*). Other coating compositions were prepared from an oil-modified alkyd, the ester of an aliphatic polycarboxylic alkyne oxide with a polyhydric alcohol, and a polyacrylamide (Spencer, *U. S. 2,965,588*); an oil-modified alkyd, an etherified or unetherified melamine resin, and an etherified or unetherified N-substituted melamine resin (Culbertson and Williams, *U. S. 2,980,636-7*); and an epoxidized oil, a cellulose derivative, and an alkanol-modified urea, melamine, or benzoguanamine resin (Coney et al., *U. S. 3,003,987*).

The preparation of linear acrylic copolymers capable of reacting with amino-formaldehyde resins to yield novel thermosetting systems was described (Petropoulos, *Offic. Dig., Federation Soc. Paint Technol.*, 33, 719). Alkyd copolymers based on acrylic, styrene, and vinyl toluene monomers as well as epoxy and silicone materials have been developed as vehicles for solvent coating systems (Whold, *Ibid.*, 33, 220).

Factors that simplify and shorten the calculation of almost any type of phthalic alkyd resin formulation are tabulated, and equations to expand the tables further are given. (Glaser, *Ibid.*, 33, 62). Calculations are presented for a practical means of formulating isophthalic resins duplicating functionality characteristics of phthalic alkyds (Brown and Ashjian, *Ibid.*, 33, 539). A study has been made of the effects of *cis*-1,2-cyclohexane-dicarboxylic or hexahydrophthalic anhydride on properties of alkyd resins. Properties of coatings based on hexahydrophthalic alkyds are given (Berger and Kane, *Ibid.*, 33, 579). A study of the influence of excess polyalcohol and dimerization of the fatty acid chains on the film properties

of drying oil-modified alkyd resins showed that dimerization contributes strongly to the viscosity but exercises no influence on the film properties (Bult, *Ibid.*, 33, 1594). The effect of adding oxygenated solvents to hydrocarbons used as solvents for a short oil alkyd was studied (Seneker, *Ibid.*, 33, 1329). Advances made in the field of high temperature coatings and properties of unmodified silicone coatings, silicone-ceramic hybrids, and silicone alkyd copolymers are covered (Glaser et al., *Ibid.*, 33, 1197). The importance of silicones in industrial finishes and their applications are discussed and illustrated (Cahn, *Ibid.*, 33, 607). The problem of evaluating a new polyfunctional product such as trimethylolpropane and its applications in alkyd resins was discussed (Wiech, *Ibid.*, 33, 120).

Alcohols derived from unsaturated fatty acids can be converted into polymeric materials by first converting them into polymerizable ethers or esters. A review described the preparation of fatty vinyl ethers and the copolymerization of these ethers with fatty oils, and other fatty derivatives and chemicals (Uzzan, *Rev. Franc. Corp. Gras, Spec. No.*, April 28, 1960, 13). Vinyl ethers of stearyl, oleyl, and linseed alcohols were prepared by the acid-catalyzed addition of each alcohol to ethyl vinyl ether to form an unsymmetrical acetal, followed by cleavage of the acetal to yield ethanol and the fatty vinyl ether (Dejarlais et al., *JAOCs*, 38, 241). Materials capable of being molded were obtained by copolymerization of acrylonitrile with octadecyl acrylate and other alkyd acrylates (Jordon et al., *Ibid.*, 231). A series of urethanes containing fatty groups on both the oxygen and nitrogen atoms were prepared by reaction of fatty alcohols with fatty isocyanates. The urethanes gave thixotropic gels at concentrations as low as 0.5% in ethyl alcohol, soybean oil, and solvent-thinned resins (Shulman et al., *Ibid.*, 205).

The following resins prepared without the use of fatty drying oils were described: thermosetting appliance finishes from acidic copolymers cross-linked with diepoxides (Murdock and Segall, *Ind. Eng. Chem.* 53, 465); baked finishes from acrylamide interpolymers, alone or with other resins (Vogel and Bittle, *Ibid.*, 461); thermosetting materials from acrylamide interpolymers and formaldehyde (Christenson and Hart, *Ibid.*, 459); thermosetting coatings from amino resins and acrylic copolymers containing functional groups capable of reaction with the amino resins (Petropoulos et al., *Ibid.*, 466); thermosetting materials from acrylic interpolymers and epoxy resins (Applegath, *Ibid.*, 463); phenolic resins suitable for punching, internally plasticized by the introduction of alkyd substituents, the most effective of which was *m*-isopropyl (Freeman and Traynor, *Ibid.*, 573); and internally plasticized phenolic molding resins and laminating varnishes prepared by alkylation of phenol with a chlorinated paraffin wax, treatment with formaldehyde, and condensation with phenol under acidic conditions (Brookes, *Ibid.*, 570).

The following papers were presented in a symposium on thermosetting acrylic resins (Gerhart, *Offic. Dig., Federation Soc. Paint Technol.*, 33, 678): Thermosetting Compositions from the Reaction of Acrylamide Interpolymers with Formaldehyde (Christensen and Hart, *Ibid.*, 33, 684); Coatings Based on Acrylamide Interpolymers (Vogel and Bittle, *Ibid.*, 33, 699); Thermosetting Compositions Based on Acidic Copolymers Cross-Linked with Diepoxides (Murdock and Segall, *Ibid.*, 33, 709); Acrylic Coatings Cross-Linked with Amino Resins (Petropoulos et al., *Ibid.*, 33, 719). Methods of formulation and effect of formulation variables upon film properties of thermosetting acrylic resins and their application conditions were reviewed (Graeff et al., *Ibid.*, 33, 345). The role of epoxy resins as curing agents for thermosetting resins was discussed (Applegath, *Ibid.*, 33, 737).

Miscellaneous formulations involving drying oil products for protective coatings and related uses included the following: a drying or semidrying oil containing up to 2% of a diazine compound as a drier (Bloom, *U. S. 3,005,789*); boiled linseed oil containing red lead and a zinc salt reaction product of lecithin (Kronstein and Eichberg, *U. S. 2,997,398*); a drying oil-rosin-phthalic anhydride-glycerol alkyd containing finely divided non-leaving aluminum particles (Polorina, *U. S. 2,980,638*); a paint latex containing heat-bodied linseed oil, a hydrocarbon solvent, and an oxyalkylated monoalcohol in the disperse phase water, a non-ionic emulsifier, and an alkali salt of a polymerized fatty acid in the continuous phase (Penoyer, *U. S. 2,978,346*); a coating for magnesium metal articles consisting of a hydrocarbon oil or a fatty oil, and a hydroxy compound such as glycol or carbohydrate (Palumbo, *U. S. 3,004,869*); a water-repellent composition consisting of a styrenated castor-phthalic anhydride-glycerol alkyd, a film hardener, a small amount of paraffin wax, and a solvent (Fain and Goldman, *U. S. 2,967,163*); a paint tinting color base consisting of dehydrated castor oil, soybean lecithin, pigment, and a nonionic surfactant (Seeker, *U. S. 2,996,397*); a metal

primer consisting of an air-drying vehicle, an anti-corrosive pigment, and, as a wetting agent, an ester of a drying oil acid with an aliphatic monohydric alcohol having up to eight carbon atoms (Long and Shobe, *U. S. 2,978,424*); a road marking paint consisting of glass particles suspended in a drying oil varnish vehicle or in an oil-modified alkyd resin (Wynn and Huntzicker, *U. S. 3,005,790*); and a heat and weather resistant paint consisting of finely divided molybdenite dispersed in linseed oil (Rushton and Rushton, *U. S. 2,956,897*). The use of linseed oil for winter protection of concrete road surfaces and garage floors was described (Morris, *JAACS*, 38, No. 5, supp. 24).

Lecithin was phosphorylated or made to react with Co, Pb, Ni, Mn, Fe, Zn, or Ti, hydroxides or carbonates to give lecithinate which can be used in pigmented coatings to decrease drying time and impart other desirable properties (Kronstein and Eichberg, *U. S. 2,997,398*).

A procedure for testing the effectiveness of a primer as a barrier between an alkaline substrate and alkali-sensitive top coat was described (Lauren, *Offic. Dig., Federation Socs. Paint Technol.*, 33, 1346). Aqueous emulsions of heat bodied linseed oil containing TiO_2 pigment and various minor components were evaluated as paints (Schwab et al., *Ibid.*, 33, 747). Preparation of varnishes made from liquid epoxy resin ERL-2774, bisphenol A and drying oil fatty acids have been described (Richardson and Wertz, *Ibid.*, 33, 1310).

The exposure characteristics of white and colored linseed oil house paints containing wollastonite, magnesium silicate and calcium carbonate were given (Roemelt, *Ibid.*, 33, 95). Drying oil esters of sucrose were prepared by catalytic ester exchange between sucrose and methyl esters of linseed oil (Bobalek, *Ibid.*, 33, 453).

The composition and physical characteristics of basic lead silico chromate, an anti-corrosive pigment were discussed (Bates and Whitney, *Ibid.*, 33, 27). A review covered the use of basic pigments used in paints (Walker, *Ibid.*, 33, 481). Properties such as electrosmosis, water vapor and hydrogen permeability, tensile strength and elongation, and reaction to constant stresses were studied for several types of paints (MacDonald, *Ibid.*, 33, 7).

The problems of post-mixing and some of the factors that affect the uniformity of a finished paint were discussed (Daniel, *Ibid.*, 33, 830). A new method for utilizing the previously published "Oil Contribution Curves" of ten pigments, five whites and five extenders, to calculate the critical pigment volume concentration (C-PVC) of various proportions of any combination of these pigments has been developed (Eugler, *Ibid.*, 33, 1437). A relationship between the PVC of a formulation and the C-PVC of its pigmentation was derived which may be used by the formulator to predict the porosity of the paint film. This porosity index was also shown to be a means of expressing the rate at which a given pigmentation developed dry hiding power with increasing porosity (Stieg and Ensminger, *Ibid.*, 792). Principles of formulation of ordinary and specialty paints were reviewed (Mills, *Paint, Oil and Colour J.*, 139, 456, 767, 1000, 1247, 1558; 140, 203).

A series of six papers on "Exterior House Paints" was published: Introduction (Vannoy, *Offic. Dig., Federation Socs. Paint Technol.*, 33, 1611); Acrylic Emulsion House Paint (Allyn, *Ibid.*, 1615); New Substrates for House Paints (Anderson, *Ibid.*, 1618); Water-Soluble Oil House Paints (Farstad, *Ibid.*, 1625); PVAc Emulsion House Paints (Fickenschel, *Ibid.*, 1630); Alkyd House Paints (Fortener, *Ibid.*, 1634).

Fundamentals of emulsion polymerization and significant new approaches were reviewed (Naidus, *Ibid.*, 1582). Exposure results using various latex paints over wood surfaces were discussed (Vannoy, *Ibid.*, 807). Exposure performance of oil, alkyd, and emulsion paints containing different extenders was described (Vannoy, *Ibid.*, 33, 25). A study of the behavior of nine different and distinct emulsion vehicle systems pigmented at four levels of pigment volume, applied over ten different substrates and exposed south vertical for years was reported (Toothill, *Ibid.*, 33, 1453). The performance of PVA paints over both wood and cementitious surfaces was comprehensively evaluated as a function of binder, extender pigments, PVC and substrate (Tiherti, *Ibid.*, 33, 390). The problem of grain cracking in PVA paints was discussed (Taffe and Fickenschel, *Ibid.*, 33, 331). A study of the latexes obtained by copolymerizing vinyl acetate with a variety of acrylates and the films or paints prepared from them has been made (Cogan, *Ibid.*, 33, 365). Properties and limitations of water-dispersed industrial coatings have been described (Estrada, *Ibid.*, 33, 417).

Surveys of the fat and oil market situation emphasized the importance of plasticizers from fats (*Chem. Eng.*, 67, no. 24, 90; Poats and Sills, *JAACS*, 38, no. 8, supp. 23). The preparation and use of hydroxylated and epoxidized fats as plas-

ticizers was reviewed (Naudet, *Rev. Franc. Corp. Gras, Special No.*, April 28, 1960, 7). Epoxidation of maleinized sperm acids and maleinized erucic acid was difficult, the products having oxirane oxygen contents of only 0.2-0.4%. Both the maleinized esters and their epoxides were primary plasticizers for a polyvinyl chloride, the epoxidized materials showing the better properties (Komori et al., *Yukagaku* 10, 18). Eleven esters and epoxides of maleic and acrylic acid adducts of conjugated linoleic acid and eight esters and epoxides of maleic and acrylic ester adducts of vegetable oils were evaluated as plasticizers in polyvinyl chloride, polyvinylidene chloride, and acrylonitrile rubber. The dimethyl ester of the acrylic adduct of linoleic acid and its epoxide were the best plasticizers in polyvinyl chloride. The vegetable oil adduct ester and epoxides were incompatible with polyvinyl chloride but had good compatibility with acrylonitrile rubber (Teeter et al., *JAACS*, 38, 117). Other epoxidized materials used as vinyl plasticizers were epoxidized triglyceride vegetable oil (Rowland and Conyne, *U. S. 2,963,455*), epoxidized sperm blubber oil, and the epoxidized wax from that oil (Tsteishi et al., *Kogyo Kagaku Zasshi* 64, 1028).

The morpholides of lauric, palmitic, elaidic, epoxyoleic (Magne et al., *JAACS*, 38, 294), selectively hydrogenated cottonseed, and epoxidized cottonseed acids (Magne et al., *Ibid.*, 291) were evaluated as plasticizers in vinyl resins. The latter two materials, in addition to being good primary vinyl plasticizers, were acceptable as plasticizers for cellulose triacetate and possibly as softeners for Buna A. A number of morpholides of ricinoleic acid, and other hydroxy acids and their derivatives, were patented as plasticizers for cellulose acetate and vinyl resins, as was 1,12-di- β -cyanoethoxy-9-octadecene (Dupuy et al., *U. S. 2,971,855*). Other materials described as vinyl plasticizers were a triglyceride of chlorinated coconut acids (Dohr and Krause, *U. S. 2,969,339*), and the mono and diesters of carboxystearic acid (prepared by carboxylation of oleic acid with carbon monoxide) (Roe et al., *JAACS*, 38, 527). Monohydric alcohol esters of tall oil fatty acids were described as chemical intermediates for the separation of plasticizers, cutting oils, hydraulic fluids, and lubricants (Bauer et al., *Ibid.*, 127).

The divinyl sulfone adducts of methyl α -eleostearate, of its hydrogenated derivative, and of tung oil were satisfactory primary plasticizers for nitrile rubber (Placek et al., *Ibid.*, 107). The basic lead soaps of stearic, palmitic, and oleic acids were stabilizers for vinyl resins (Kebrieh, *U. S. 3,002,943*).

Miscellaneous products containing fatty materials included a coresand containing a drying oil as a binder and lead dioxide as a setting accelerator (Schmit and Cassart, *U. S. 2,993,796*); a fibrous hardboard containing a polymerized drying oil (Young and Majka, *U. S. 2,978,382*); an aqueous liquid color containing emulsified fatty oil, polyalcohol, organic capillary active agent, emulsifiable synthetic resin, and dye (Funahashi, *U. S. 2,992,198*); a fatty monoacylide aqueous gel (Brokaw and Lyman, *U. S. 2,976,251*); a thixotropic oleaginous composition containing a minor amount of the reaction products of an abietyl amine, an organic phosphate, and a fatty acid (Eisenhauer and Zajac, *U. S. 3,000,820*); a lubricant coating for plastic surfaces consisting of an aqueous dispersion of zinc stearate and a fatty monoester of a polyethylene glycol (Price, *U. S. 2,965,589*); a mixture of zinc stearate and an epoxy resin (Cunder and Licata, *U. S. 2,972,590*); and a halogenated rubbery copolymer containing as a stabilizer an alkaline earth salt of a 5-30 carbon fatty acid (Eby et al., *U. S. 2,953,667*).

ANALYTICAL Standard methods and apparatus for testing paints and varnishes were reviewed (Huesa, *Grasas y Aceites* 11, 180). The acids from oxidized oils were separated by liquid-partition chromatography into three fractions: unoxidized acids, dimeric or polymeric acids, and a polar fraction (Frankel et al., *JAACS*, 38, 130). The same method, applied to autoxidized fatty acids or their methyl esters, separated hydroperoxides from unoxidized acids or esters (Frankel et al., *Ibid.*, 134). Fatty acids from alkyd resins were identified by paper chromatography (Kaufmann and Buscher, *Fette, Seifen, Anstrichmittel*, 62, 1141). The Zeisel method and gas chromatography were applied to the determination of alkoxy groups in polymers and copolymers containing alkyd acrylates and maleates. These methods were also applied to the determination of ester plasticizers in plastic formulations (Miller et al., *Anal. Chem.*, 33, 677). An accelerated test for the yellowing tendency of drying oils involved holding the oil, absorbed on filter paper, in air at 50C and following the color change by reflectance measurements (Privett et al., *JAACS*, 38, 27). It was concluded that the yellowing of oil films was not related directly to the drying process, but that colorless precursors of the yellow compounds were formed during oxidation of the films. The presence of low molecular weight aldehydes prevented yellowing, possibly by reacting as a sub-

stitute for one of the reactants in the color-forming reaction (Privett et al., *Ibid.*, 22). Principles of trichromatic colorimetry and the use of the CIE system in the paint industry for color measurement and specification were discussed (Seerest, *Offic. Dig., Federation Soc. Paint Technol.*, 33, 583).

Methods for the measurement of emissivity and deflectivity of organic coatings were described (Story, *Ibid.*, 33, 283). The problem of evaluating paints for resistance to mildew was reviewed and a bioassay technique as a guide for determining the performance of coatings under varied service conditions was described (Ramp and Grier, *Ibid.*, 33, 1073). Recent work on the theoretical aspects of the viscosity of dispersed systems is discussed in the light of practical paint technology. [Suggestions are made as to how basic concepts can be most readily used to the advantage of the paint chemist (Asbeck, *Ibid.*, 33, 65).] Viscosity is used to follow the course of the thermal polymerization of drying oils and of the manufacture of alkyd resins (Hutchinson, *J. Oil and Colour Chemists' Assoc.*, 42, 283). Qualitative and quantitative analysis of solvents in automotive lacquers is accomplished by programmed temperature gas chromatography without prior distillation of solvent (Esposito and Swann, *Offic. Dig., Federation Soc. Paint Technol.*, 33, 1122). Gas chromatography techniques have been adapted to determine the presence and quantitative character of solvents in a film. The effects of vehicle composition, solvent types, film dimensions, ambient and elevated temperature exposures, and other treatment variables have been considered. A correlation of film solvent content and film hardness has been carried out (Murdock and Carney, *Ibid.*, 33, 181). Gas chromatography was employed for the qualitative determination of oil content in organic coatings (*Ibid.*, 33, 622). The use of infrared spectroscopy as an analytical tool in the field of paints and coatings was discussed (Brown et al., *Ibid.*, 33, March, pt. 2, 160 pp.). A method based on exposure to ultra-violet light under specified conditions, as a means of determining suitability of the gloss retention of certain paints, and the apparatus have been described (Sawyer, *Ibid.*, 33, 268). Optical analytical techniques, with emphasis on infrared analysis, as tools for studying and characterizing coating vehicles have also been described (Pervetti and Miller, *Ibid.*, 33, 1006). Applications of microscopy (McCrone, *Ibid.*, 33, 40), X-ray methods (Leibhafsky and Welbon, *Ibid.*, 33, 42), and applications of instrumentation (Brenner, *Ibid.*, 33, 51) in the paint industry were discussed. A new microanalytical, radioactive method for the estimation of the iodine number in linseed oil was reported (Abdel-Wahab and El-kinawi, *Z. Anal. Chem.*, 180, 420).

PRODUCTION PROCESSES

EXTRACTION

Four patents of new extraction equipment were issued during the year. An apparatus for extraction of oil from rice bran consisted of a tank with a liquid pervious support extending horizontally in the tank to hold a batch of bran. The bed of bran remained undisturbed during the entire period of extraction (Mickus and Brewer, *U. S. 2,990,255*). In a sonic extractor for continuous production of vegetable and animal fats and oils, the moisture content of the material was increased to reduce the binding power between cell parts and oil to a minimum. The liquid oil itself served as carrier for the alternating pressure impulses (Petter, *Ger. (East)* 20,312). Paste formation in the extraction of starchy oilseeds was prevented in a newly designed apparatus (Pintsch-Bamag A. G., *Ger. 1,062,375*). Continuous countercurrent extraction of vegetable oils was accomplished with a new extraction unit (Kichigin, *U.S.S.R. 134,358*).

Several new or modified extraction processes were reported. Cottonseed oil was obtained free of gossypol and fatty acids by two-stage extraction of cottonseed pulp with an acetone-water mixture containing 50–85% acetone (Markman et al., *U. S. S. R. 134,359*). In a multistage countercurrent extraction process for vegetable oils, a miscelle containing 60–85% oil was obtained by extracting at a temperature slightly above the boiling point of the solvent (Neshehadini, *U. S. S. R. 134,361*). Olive oil was extracted by first squeezing the olive pulp in a hydraulic press followed by continuous solvent extraction in a countercurrent fluidized-bed column (Giorgi, *Ital. 554,405*). A method for dehydration of miscella obtained by extraction of oils with water-miscible solvents was reported (Paul, *Fr. 1,187,227*).

Greater oil yields were obtained by solvent extraction of unhulled rather than hulled cottonseed (Ivanov, *Tekh-Ekon. Byull. Sovet. Narod. Khoz. Fergansk. Ekon. Admin. Raiona*, No. 1, 14–15 (1948). Acetone-hexane-water mixture was shown to be an efficient solvent for extraction of oil and gossypol

from raw cottonseed meats (King and Frampton, *JAACS*, 38, 497–499 (1961).

A simple and inexpensive modification of the filtration-extraction process involves an additional soaking step. This permits improved extraction efficiency and reduced solvent requirements (D'Aquin, et al., *JAACS*, 38, 258–261 (1961). Filtration-extraction has been successfully applied on a laboratory-scale to extract whole or decorticated safflower seed (E. L. D'Aquin, et al., *JAACS*, 38, 44–47 (1961).

The effect of temperature on denaturation of protein substances and on the content of amino acids in the process of oil extraction from soybean was investigated (E. Ya. Nedel'ko, *Biol. Resursy Dal'n Vost Sbornik*, 162–70 (1959). The influence of flow rate on the quantity of solvent required for extraction of oil from rape seed cake was discussed (Jackubowski and Katzer, *Prace Inst. i lab Badawczych Przemysl. Rolnego i Spozyczego* 10, No. 3, 63–72 (1960). Studies on mass exchange during the extraction of oil from olive were reported (Rizaev, et al., *Izvest. Vysshiki Ucheb. Zavedeni, Khim. i Khim Tekhnol.*, 3, 933–936 (1960). No difference was found in the fatty acid composition of the glyceride portion of hexane extracted cottonseed oil obtained at various stages of solvent extraction (Arnold and Choudhury, *JAACS*, 38, 87–88 (1961). The refining loss, phospholipid content and color of the hexane extracted oil increased as the residual oil content of the meal decreased (Arnold, et al., *JAACS*, 38, 336–338 (1961).

REFINING

Several refining processes were reported. Fatty oils were refined by mixing the oil with a suitable aqueous alkaline reagent followed by centrifugal separation (Ayres, *U. S. 3,004,050*). Deacidification of vegetable or animal fat was achieved by filtration through special "synthetic resins" (Mentasti, *Ital. 565,276*). Refining loss of 1.1–1.3 times the F.F.A. content, was obtained when oils were refined with alcoholic alkali (Rebello and Shitole, *J. Sci. Ind. Research (India)*, 20 D, 179–186 (1961).

Refining in vacuum using a process temperature of 40–60°C yields an improved refined oil (Brücke, *Ger. 1,093,934*). A commercial unit for continuous refining of fats and oils consists of a battery of jacketed cylindrical vessels, connected in series, which hold alkaline solution. The crude oil was injected in a fine stream at the bottom of each vessel (Kominski, et al., *U.S.S.R. 130,140*). DeSmets' continuous refining process consists of washing hexane solution of the oil with a solution of sodium hydroxide in aqueous isopropyl alcohol (Vander Woort and Debrus, *Riv. Ital. Sostanze grasse* 38, 239–245 (1961). Neutralization of oils and fats was accomplished in acetone or dioxane solution (Vaccarino and Vaccarino, *Ger. 1,087,306*). Typical plant-operating data, for continuous degumming, refining and water washing of soybean oil, for a Duozon and Hydraron "in series" were presented (Kaiser and Hoffman, *JAACS*, 38, 332–335 (1961).

Use of *o*-aminobenzoic acid instead of *p*-aminobenzoic acid to remove gossypol from cottonseed oil permitted process and product improvements (Rzhekhin and Belova, *Mastoboino Zhirovaya Prom. 27*, No. 1, 12–15 (1961). Gossypol and related pigments were removed as borate complexes from crude cottonseed oil which was then alkali refined (Council of Sci. Ind. Research (India), *Brit. 852,721*). Addition of PO_4^{3-} or NH_4^+ or both afforded better separation of neutral oil and soap stock in alkali refining of fats and oils (Mitani, *Japan 13,392*).

Optimal conditions for deacidification of natural and hardened oils were examined (Fiala, *Prumysl Portravin*, 12, 342–346 (1961). Laboratory refining of U. S. Soybean oil showed no relationship between FFA content and refining loss (de Castro and Nosti, *Grasas y Aceites*, 11, 213–219 (1960). High FFA olive oils were deacidified by esterification with glycerol, under reduced pressure using 0.2% zinc catalyst (Ruiz and Ramos, *Grasas y Aceites*, 12, 16–18 (1961).

Methods for degumming include a process for soybean oil in which a solution of the oil in a suitable solvent is treated at 130°F with 1½ to 2½% each of water and alcohol (Cavanagh and Bean, *U. S. 2,980,718*); and another process for rape seed oil (Guillumin and Boulot, *Rev. franc Corps gras*, 7, 506–519 (1960). A process to degum cottonseed oil with water was investigated (Burnasheva and Sterlin, *Mastoboino Zhirovaya Prom.*, 26, No. 11, 18–21 (1960).

BLEACHING

Equipment for continuous bleaching of oils consisted essentially of a flow regulator for oil, a vessel fitted with a stirrer and a continuous rotary filter (Kraus-Maffei A-G, *Ger. 1,056,765*). Continuous purification and decolorization of oils were effected by subjecting the fluid mixture of crude stock plus

bleaching adsorbent to a sudden rise in temperature at sub-atmospheric pressure and then by allowing the materials to fall countercurrent to a rising stream of superheated steam (Raffaeta, *U. S. 2,980,717*). Vegetable oils were decolorized by treatment with activated carbon containing 15–60% water and either 5–10% of hydrochloric acid or less than 3% sodium hydroxide (Lab. für Adsorptionstechnik, G.m.b.H., *Ger. 1,103,490*).

Activated alumina was found to be superior to several other adsorbents in removing the fixed red pigments from refined off-colored cottonseed oil (Pons et al., *JAOCs*, 38, 104–107 (1961)). The bleaching capacity of activated clays was higher at atmospheric pressure (air or nitrogen) than in vacuum (Fontana and Burana, *Cultivatore*, 106, 213–216 (1960)). Acid activation and bleaching capacity of "gumbrin" were studied (Bariabishvili, et al., *Trudy Inst. Khim., Akad. Nauk. Gruzii. S.S.R.*, 14, 37–52 (1958)). Laboratory tests for evaluating the quality and efficiency of bleaching earths were reviewed (de Castro, *Grasas y Aceites*, 12, 23–32 (1961)).

DEODORIZATION, WINTERIZATION AND FRACTIONATION

An equipment was patented for simultaneous deodorization and neutralization of vegetable oils by distillation of uncombined fatty acids (Bloemen, *Fr. 1,233,792*). Another patent related to steam deodorization of vegetable or animal fats at a temperature of 425–30F for 2–3 hr (Armour and Co., *Brit. 844,809*).

A process for cottonseed oil winterization by fractional crystallization from a solvent consisted of rapidly chilling to 0C a mixture of oil and 10% by wt of solvent. The mixture was held at that temperature for 3–4 hr followed by separation of the solids by centrifugation (Mertens, et al., *JAOCs*, 38, 286–289 (1961)). An apparatus for destearinating cottonseed oil in miscella was described (Perepelyuk, *Tekhn. Ekono. Byull. Sovet. Narod. Khoz. Fergansk. Ekon. Admin. Raiona* No. 1, 16–17 (1958)).

95% pure linolenic acid was produced by liquid-liquid extraction of linseed oil fatty acids with wet furfural and hexane in Podbielniak centrifugal extractor. The minimum ratio of furfural to acids to obtain this purity was 10 to 1 (Beal, et al., *JAOCs*, 48, 524–527 (1961)). Monoglycerides were separated from glycerol by precipitation with cold water (Henkel & Cie. G.m.b.H., *Ger. 1,066,573*). Cottonseed oil pigments were fractionated by means of molecular sieves, countercurrent distribution and low temperature crystallization. The three techniques gave very similar pigment fractions (Verberg et al., *JAOCs*, 38, 33–39 (1961)).

Complete separation of β -elaeostearic acid from a mixture of α - and β -elaeostearic acids was obtained by repeated treatments of the mixture with urea in methyl alcohol (Rankov, et al., *compt. rend. acad. bulgare Sci.*, 13, 71–74 (1960)). Suitable conditions were reported for separating fatty acids from tall oil with urea (Van'yan, *Masloboino-Zhirovaya Prom.*, 26, No. 9, 28–30 (1960)). Fractionation of rice oil fatty acids by extractive crystallization with urea was reported (Mehta and Meshramkar, *Indian Oil and Soap J.*, 26, 18–21 (1960)). The use of urea adducts for the separation of mixtures of fatty acids, esters, and waxes was discussed (Srivastava, *Indian Oil and Soap J.*, 3, 51–55 (1960)).

HARDENING

Mass transfer processes determine the rates of hydrogenation of oils with Ni-SiO₂ as catalyst. Hydrogen transfer was the most important (Coenem, *Actes Congr. intern. catalyse*, 2^e, Paris 2705–2729 (1960)). Kinetics and reaction mechanism of hydrogenation of sunflower oil in solution was reported (Golodova, et al., *Trudy Inst. Khim. Nauk Kazakh S.S.R.*, 5, 44–49 (1959)).

During hydrogenation of sunflower oil with formate-nickel catalyst, no significant loss of selectivity was observed when the catalyst concentration was increased from 0.075 to 0.15% (Kolesnikov, *Trudy Krasnodar Inst. Pishchevoi Prom.* No. 13, 23–26 (1957)). The influence of temperature, catalyst concentration and hydrogen flow rate on the formation of position isomers during hydrogenation of soybean oil was discussed. Increase in the quantity of nickel catalyst and decrease in hydrogen flow rate increase the formation of solid isooleic acid (Pavlov and Poddubnyi, *Izvet. Vysshikh Ucheb Zavedeni, Pishchevaya Tekhnol.*, No. 5, 42–48 (1960); No. 3, 68–61 (1961)).

The overall rate of hydrogenation was directly proportional to the degree of unsaturation of the oil and to the amount of Ni catalyst used. The rate increased with increasing pressure and temperature, but selectivity and isomerization decreased with increasing pressure (Wisniak and Albright, *Ind. Eng.*

Chem., 53, 375–380 (1961)). Catalyst concentration, solvent, temperature and pressure had very little effect on the selectivity of hydrogenation of linolenic acid. However, large differences existed in the relative reactivities of the three double bonds in methyl linoleate. The double bond at 12 position was the most reactive (Willard and Martinez, *JAOCs*, 38, 282–286 (1961)). During continuous hydrogenation of oils, higher efficiency was reported in a three stage as against a two stage autoclave battery (Beznosov, *Trudy Krasnodarsk. Inst. Pishchevoi Prom.* No. 15, 103–108 (1957)).

Glycerides were hydrogenated by passing the miscella from solvent extraction over a nickel-aluminum or nickel copper alloy supported on silica gel (Kaufmann, *Brit. 870,393*). The data on hydrogenation at atmospheric pressure of teaseed, poppyseed and nigerseed oils were reported (Basu and Chakrabarthi, *J. Sci. Ind. Research (India)*, 19B, 227–228 (1960)). During hydrogenation of the oil of *Hydnocarpus Wightiana*, which is rich in cyclopentenyl fatty acids, optical inactivation was produced by a shift in the double bond (Kamath and Kane, *Proc. fourth symposium on fats, oils and allied products*, 1955). Hydrogenation conditions for oiticica oil were studied (Kaufmann and Sud, *Fette, Seifen, Anstrichmittel*, 63, 138–147 (1961)). X-ray diffraction data showed that Cu-Cr-Mn oxide catalyst which was used in the hydrogenation of oils contained cupric oxide reduced to metallic copper. The spent catalyst was regenerated by the wet oxidizing method (Takumi and Hashimoto, *Yukagaku*, 10, 150–153 (1961)).

A hardened fat, free of iso acids, was obtained by hydrogenation of animal fat in solution using the usual catalysts and a temperature below the boiling point of the solvent (Kaufmann, *Ger. 1,076,300*).

INTERESTERIFICATION

A cocoa butter-like fat was prepared by interesterification of hydrogenated cottonseed oil with a triolein product, or with olive oil followed by fractional crystallization from acetone at two different temperatures (Spadaro, et al., *JAOCs*, 38, 461–465 (1961)). Undirected and directed interesterification of tallow, with 0.3% sodium methoxide as a catalyst, were carried out in a nitrogen atmosphere to inhibit discoloration of the product (Nakazawa, et al., *Yukagaku*, 6, 156–160 (1957)).

The effect of time and temperature, on the type of end product which was produced during the interesterification of lard with sodium methoxide catalyst, was discussed (Wiedermann, et al., *JAOCs*, 38, 389–395 (1961)). The mechanism of interesterification reaction was studied. The over-all reaction can be broken down to three phases. In the first phase the sodium methoxide reacts with the fat to form an active catalyst. The second phase was characterized by a permanent and complete change in crystal structure. During the last phase the fatty acids of the triglycerides approach random distribution (Weiss, et al., *JAOCs*, 38, 396–399 (1961)).

Directed interesterification of fats were reviewed with 19 references (Solomon, *Rev. franc. Corps. gras.*, 8, 221–227 (1961)).

PARTIAL ESTERS AND FAT SPLITTING

Diglycerides were prepared by reacting the fat with glycerine in the presence of 0.02–1.0% catalyst (Seestorm, et al., *U. S. 2,999,021*). The synthesis of mixed diglycerides in any one of the four theoretically possible forms was carried out (Buchnea and Baer, *J. Lipid Research*, 1, 405–411 (1960)). Pilot plant batches of 30–47 lb of tung oil were reacted with excess of glycerol in the presence of sodium methoxide catalyst to obtain a product containing 32–45% monoglycerides. The unreacted glycerol was removed from the product by centrifugation (Eaves, et al., *JAOCs*, 38, 443–447 (1961)).

Toluene sulfonic acid was used as catalyst to esterify pure tall oil fatty acids with butyl and higher monohydric alcohols. These esters were low in acidic impurities and light in color (Bauer, et al., *JAOCs*, 38, 127–130 (1961)). Fatty acids derived from different oils were reacted with epichlorohydrin in the presence of quaternary ammonium halides to produce glycidyl esters in 80–95% yields (Maerker, et al., *JAOCs*, 38, 194–197 (1961)). Preparation of some diacid asymmetric triglycerides was reported (Taufel, et al., *Fette, Seifen, Anstrichmittel*, 62, 926–928 (1960)).

The amount of monoglycerides, formed by hydrolysis of fat in a homogeneous system, agrees with the theoretical amount calculated on the basis of random esterification (Peredi, *Fette, Seifen, Anstrichmittel*, 62, 1034–1038 (1960)). A method to calculate the "coefficient of incompleteness" which characterizes the concentration of the intermediate products in partially hydrolyzed fat was given (Molchanov, *Trudy Krasnodarsk. Inst. Pishchevoi Prom.* No. 20, 111–114, (1958)).

96–97% hydrolysis was achieved in Petrov continuous fat splitting process using "Sulphophenic" and sulphuric acids

as catalyst (Bespyatov, *Trudy Khar'kov Politekhn. Inst. im V. I. Lenina, Ser. Khim. Tekhnol.* 13, No. 4, 105-110 (1957). The negative catalysts present in rancid oils brought about a rapid decrease in the amount of Twitchell reagent during hydrolysis of the oils (Kanno, *Kogyo Kagaku Zasshi*, 64, 311-315 (1961).

VEGETABLE AND ANIMAL FATS AND OILS

Reviews were published on modern technology of fats and fatty products and high pressure method of oil extraction (Kaufmann and Grothues, *Fette, Seifen, Anstrichmittel*, 62, 1085-1090 (1960); Products from sunflower seed (Mizuno and Guerrero, *Rev. Arg. de Grasas y Aceites*, 3, 39-44 (1961); the relationship between hull content of sunflower seed kernel and oil losses during processing (Matsuk, *Masloboino-Thirovaya Prom.* 27, No. 1, 7-10 (1961); and castor oil processing and industrial utilization of by-products (Geleji, et al., *Maguar Kem. Lapja*, 15, 298-303 (1960).

The industrial uses of castor oil were discussed (Iovchev, *Priroda (Sotia)*, 6, No. 6, 57-59 (1957). Recent inventions in the field of oils and fats were surveyed (*oils and oil-seeds J.*, (India) 9, No. 11, 10-12 (1957). Various aspects of palm oil industry were described (Raymond, *Tropical Sci.*, 3, 69-89 (1961).

Refining and bleaching in air decreased the stability of olive oil (Nosti and de la Borbolla, *Grasas y Aceites* 11, 139-150 (1960). Changes in the quality of cottonseed oil during storage were discussed (Sterlin and Burnasheva, *Uzbek. Khim. Zhur.* No. 3, 54-57 (1960).

Optimum conditions for processing cottonseed and soybean oils were suggested (de Castro and Ramos, *Grasas y Aceites*, 11, 97-101 (1960). The effect of the extent of milling of cottonseed meal on the oil content of the cake was investigated

(Glushenkova and Markman, *Masloboino-Zhirovaaya Prom.* 27, No. 8, 22-25 (1961).

Oil from fish, fish waste, and whale meat was recovered by disintegrating and homogenizing the material for 5-6 hr followed by centrifugation (Ehlert and Mikkelsen, *Norw.* 96,177). Inadequate filtration after rendering and contamination with iron and copper decreased the stability of lard (Vargas, et al., *Grasas y Aceites*, 11, 243-247 (1960).

BY-PRODUCTS

A semi-countercurrent process for extraction of woolwax used trichloroethylene as the solvent at a temperature of $45 \pm 2^\circ\text{C}$ (Kamada and Inone, *Yukagaku*, 5, 239-240 (1956). Waxy components were separated from sterols by extracting a mixture obtained from tall oil or crude "cane oil" with ethylene dichloride (Miller, et al., *U. S. 3,004,992*). Lecithin products were recovered from soapstocks by treatment with mineral acids at temperature and pressure insufficient to split or char the phosphatides (Thurman, *U. S. 2,970,910*). A patent was issued for the recovery of fatty material from wash water obtained during refining of vegetable oil (Allen and Wack, *U. S. 2,993,006*).

Lysine values for sesame protein from solvent extracted meal were much higher than those obtained for screw pressed meals (Carter, et al., *JAOCs*, 38, 148-150 (1961). A new process using acetone as solvent permitted the processing of cottonseed to produce a meal containing neither free nor bound gossypol (Vaccarino, *JAOCs*, 38, 143-147 (1961). Defatted soybean flakes were successfully debittered by countercurrent washing with aqueous ethyl or isopropyl alcohol. The entrained solvent was removed by flash distillation without excessive denaturation of protein (Mustakas, et al., *JAOCs*, 38, 473-478 (1961).

Mustard Seed Processing: Bland Protein Meal, Bland Oil, and Allyl Isothiocyanate as a By-product¹

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Abstract

Mustard seed like rapeseed is characterized by the presence of glucosides, which are readily hydrolyzed under certain conditions by enzymes in the seeds to produce pungent "mustard oils." This property is utilized in the preparation of condiments from some varieties of mustard, but when the seed is processed to yield a palatable oil and feed meal, this pungent factor must be removed. This was accomplished in bench-scale studies at the Northern Laboratory by converting the mustard glucoside enzymatically and removing the converted product, allyl isothiocyanate, during a subsequent cooking step before filtration-extraction of the meal.

Introduction

THE AGRONOMIC POTENTIAL of oriental mustard seed as an erucic acid-containing oilseed has been demonstrated in several parts of the world, e.g. India, Pakistan, Canada, Western Europe, Southern Italy, the Soviet Union and the United States. It is high in oil (42%) and in meal protein (46%). In this country, the seed is grown primarily for condiment purposes. Workers at this laboratory engaged in the screening of new crops for commercial development

in the United States have reported favorably on the utilization aspects and potential of oriental mustard seed (9). Nutritional values for mustard meals were recently reported as quite promising by K. J. Goering et al. (6). Opportunities for mustard seed as an oil-meal crop could develop in areas that produce a wheat surplus and particularly in areas that are rather far removed from soybean production and are in need of high-protein animal feeds. Possible uses of erucic acid oils are in industrial lubricants and as sources of the lower molecular weight cleavage products, brassylic and pelargonic acid.

Because oriental mustard seed is grown principally for a condiment, little information has been published dealing with the economic processing of the seed into oil and meal products. Also, little information is available on methods for removal of the glucosides that impart pungent factors to the oil and meal fractions. The presence of the essential oil presently limits the proportion that can be used in cattle rations. K. J. Goering has patented a process (5) for obtaining a bland feed material from mustard seed. By his method, mustard seed is first processed to separate the lipid from the glucoside-containing-meal fraction. The meal is then treated in a series of additional steps to remove the essential oil, allyl isothiocyanate. The present paper discloses a simplified process in which the glucosides are removed before the lipids are separated. This procedure eliminates many operating steps. The new process devi-

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² A laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, USDA.