

Report of the Literature Review Committee

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

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Introduction

This year, as in the past, the compilation of new literature was made from current, original publications and from abstracts of publications that were not available in the original. The literature contributions on the subject under review were about the same as in previous years, but there appears to have been a shift in interest. Published works on analysis and processing have attracted more attention while the physical, biochemical, and physiological phases of lipid chemistry have decreased somewhat. The technical uses for fat derivatives as lubricants, anti-corrosives, emulsifiers, demulsifiers, etc., have attracted more interest.

Soaps and Detergents

MANUFACTURE

Processes

Spray-drying continued to be important, and several patents appeared that offered processes to control the operation. Ester type of compounds were prepared by heating with a carboxylic acid, a salt of 2-hydroxyalkane sulfonic acid, and a catalyst in an inert atmosphere (Anderson and Schenck, *U.S. 2,923,724*). A nonionic surfactant and a hydratable alkaline builder were prepared as a free-flowing product by transfer from a spray tower to a fluidizing tower (Schauer, *U.S. 2,941,947*). Non-ionic-built detergent compositions in controlled density, spray-dried form were obtained by the addition of soaps to the slurry before drying (Fliteraft, Satkowski, Schauer, and Liss, *U.S. 2,925,390*). Caking of spray-dried soap was prevented by the addition to the builders and soap of 2 to 18% of an alkali metal xylene sulfonate (Reich and Kelly, *U.S. 2,940,935*). In contrast, a number of formulas for nonspray-dried compositions were presented (Davidsohn, *Soap Chem. Specialties*, 36 [6], 151-156, 201). High density in spray-dried product is obtained by deaerating prior to introduction into the tower (Davis, *U.S. 2,952,638*).

Other physical forms of detergents appeared. Detergent bars of fatty acid monoglyceride containing less than 1% free fatty acid were developed (Schmolka, *U.S. 2,945,816*). Continuous processing of soap bars by the Meccaniche-Moderne process requires that only those materials be used that give a hard soap. By so doing, better processing with less deformation on aging can be attained (Anon., *Indian Oil & Soap J.*, 25, 181-184). Perfuming of Mazzoni-process, continuous-bar soap was said to be less difficult with lower losses than by ordinary processes (Schmidt, *Soap, Perfumery, Cosmetics*, 33, 410-412).

Ribbons of a soap and higher fatty acid monoglyceride sulfate composition were prepared by control of the soap content to 35 to 70% of the total solids (Compa, *U.S. 2,944,977*).

Soap drying continued to demand attention. It was shown that both structural and free water are present with soda soaps (Keizo Ogino, *J. Japan Oil Chemists' Soc.*, 8, 64-68). The following structural water contents were found for the soaps: C₈ or lower acids, none; C₉, 3 mols; C₁₂, 1.75; C₁₄, 4; C₁₆, 2; C₁₈, 1; oleate, 8.34. Relationships between equilibrium water content and vapor pressure at 10 to 50°C. were measured for a number of saturated and unsaturated soaps over 10° intervals (Ezaki, Owada, and Noguchi, *J. Japan Oil Chem. Soc.*, 8, 62-64).

Neat soap was converted from grained soap by the mixing of an aqueous solution of the latter with an electrolyte, then it was separated from the mixture (Jones, *U.S. 2,902,502*). The storage properties of a soap composition from tallow, lard, coconut oil, and castor oil were found best at 0.06% free alkali

but inferior above or below this value (Chendor, *Plusce i Srodki Piorace*, 2, 213-216).

New lacquers for use in soap and detergent plants based on polyurethanes, amine-hardened epoxies, and mixed vinyl polymers are claimed to control corrosion problems (Anon., *Soap Chem. Specialties*, 35 [9], 161-163).

α -Sulfonation of palmitic, myristic, or lauric acids was accomplished by stabilized sulfur trioxide in solvent. With carbon tetrachloride as solvent, no other stabilizer was required (Ishiguro and Asahara, *J. Japan Oil Chem. Soc.*, 8, 27-30). A new sulfating agent, N-lower alkyl ethylene carbamate-sulfur trioxide, is successfully used with fatty alcohols (Smith and Harrington, *U.S. 2,957,014*).

Improvement in alkylbenzene sulfonates can be achieved by bleaching the slurry with ozone (Krems and Gray, *U.S. 2,962,526*). A salt-free sulfonated product was obtained by diluting the sulfonation slurry with ethanol to a water ratio of 50:50 or 60:40; this permitted the alkali metal sulfate to hydrate and crystallize and was followed by separation (Sullivan and Ptasinski, *U.S. 2,952,639*).

Lanolin, as the alcohol or acid, may be condensed, acylated, ethoxylated, hydrogenated, or transesterified (Wagner, *Am. Perfumer Aromat.*, 75 [7], 23-26). Lauryl ether sulfates have found many uses because of their mildness (Anon., *Indian Oil & Soap J.*, 10, 364-366).

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H. BOOK REVIEW—

Processes for the preparation of the following surfactants have been disclosed: amidothiosulfates (Gaertner, *U.S. 2,934,552*); reaction of pyridine with ethers, such as glycerylmonochlorohydrin- α -alkyl ether, to give a cationic surfactant (Kuwamura, *Kogyō Kagaku Zasshi*, 63, 973-979); higher alkyl and alkylphenol glycidyl ethers (Kuwamura, *Kogyō Kagaku Zasshi*, 63, 595-600). Also an oxirane ring-containing compound by epoxidation of a higher fatty acid (and other fatty acid derivatives) was reacted with a polyol, then with an acylation-susceptible polyamine (De Groot and Cheng, *U.S. 2,956,067*). Extraction of an alkylaryl sulfonate to remove unsulfonatable material produced a superior surfactant (Kooijman, Soorman, and Kortland, *U.S. 2,933,451*). Fatty amides of complex polypeptides, derived from proteins from scrap leather, were reacted with fatty acids (Sanders, *Soap Chem. Specialties*, 36 [1], 57-59, 122). Degraded protein treated with a halogenated acid chloride, then condensed with an amine, is said to give an effective surfactant (Sinnova, *Brit. 816,888*). Alkali metal acyl taurides may be produced as a continuous process (Walling, McKenney, and Geitz, *U.S. 2,903,466*). Reaction of two moles di-isocyanate with 1 mole dialkylamide then with polyglycol ether gives a suitable surfactant additive (Henkel and Cie., *Brit. 826,171*). Amphoteric surfactants may be prepared by the condensing of ethylene oxide with alcohols or phenols, then reacting with aminocarboxylic acids after substitution of the terminal hydroxyl groups with a halogen (Frank, *Ger. 1,013,289*).

High-molecular-weight surfactants continue to be of much interest (Oda, *Kogyō Kagaku Zasshi*, 62, 1265-1268; Yamashita and Sakai, *Yakagaku*, 9, 337-345). Polypropylene oxide-ethylene oxide surfactants were reviewed (Sato, Sonoda, and Oyamada, *Kogyō Kagaku Zasshi*, 62, 1265-1268). Polyoxyethylene derivatives of long-chain, fatty acid-sucrose esters were good surfactants with little toxicity (Kosnori, Okahara, and Okamoto, *Kogyō Kagaku Zasshi*, 63, 600-604). A single oxypropylene chain whose terminal hydroxyl group was esterified with a carboxyl acyl group gave an ester of molecular weight not exceeding 7,500 (Kirkpatrick, *U.S. 2,950,313*). New catalysts for the high polymerization of alkylene oxide were discussed (Furukawa, Tsuruta, Saegusa, Sakata, Kakogawa, Kawasaki, and Harada, *Kogyō Kagaku Zasshi*, 62, 1269-1273). An ester of a dimerized fatty acid with a polyoxyalkylene compound with a terminal hydroxyl group is prepared; the molar ratio of acid to polyoxyalkylene compound is not less than 1:1 or more than 2:1. The major proportion of the molecular weight of the polyoxyalkylene compound consists of oxyethylene to oxypropylene groups in a weight ratio not exceeding 4:1. Another patent covers the ester of an organic dicarboxy acid and a polyoxyalkylene compound (Kirkpatrick, *U.S. 2,950,299, 2,950,310*). Studies of polymerization of surfactants involved telomerization of vinyl acetate and acrylamide (Yamashita, Tsuda, Ichikawa, *Kogyō Kagaku Zasshi*, 62, 1274-1276). The polyethylation of alcohols for nonionic surfactants with the same catalyst and at the same temperature was in the order 2-ethylhexanol > lauryl > acetyl > oleyl alcohol (Ishii and Ozeki, *Kogyō Kagaku Zasshi*, 63, 1387-1390).

A composition is produced that comprises an inorganic compound and an homogeneous reaction mixture of solvent, surfactant, and the salt of an organic compound, in which the precipitated inorganic sulfate may be filtered from the reaction mixture. The specific mixture was an alkyl (C_8 to C_{18}) arylsulfonic acid, an aqueous slurry of an inorganic base, and a nonionic surfactant (Costine and Behrens, *U.S. 2,945,818*).

An aromatic compound with an alkyl side chain of C_8 to C_{18} is obtained low in inorganic salt content by spent acid removal, centrifuging, then mixing with 20% of a C_1 to C_4 aliphatic alcohol to form crystallizable sulfate with the remaining acid, then filtered off (Pengilly, *Brit. 820,340*).

Raw Materials

The entire field of raw materials used in soaps and synthetic detergents was reviewed by Machemer (*Melliand Textilber.*, 40, 56-65, 174-179). Given were much data on synthesis, properties, and patents. Branched-chain fatty acids with from 8 to 15 carbons in the chain and from 2 to 3 branched chains were synthesized through the malonic esters and magnesium organic compounds. Normal acids were generally more effective surfactants than the branched chain equivalents (Petrov, Nikischin, Ogibin, Newolin, and Tipissowa, *Fette, Seifen, und Anstrichmittel*, 61, 940-946). The general principles and practical methods of usage of fatty acids and fatty alcohols for soaps and cosmetics were discussed (Anon., *Soap, Perfumery, Cosmetics*, 33, 47-49).

The advantages of silicates for detergent building were discussed; for spray-dried products they improved quality and ease of manufacture (Schlayer, *Soap Chem. Specialties*, 35 [11],

51-54; [12], 66-67, 146). Compatibility data of silicates with polyphosphates for liquid detergents showed that the stability of these mixtures depended on the phosphate used, SiO_2 /alkali metal oxide ratio of the silicate, common ion effect, high phosphate-low silicate concentrations, high silicate concentrations, and low temperatures (Getty and Stericker, *Soap Chem. Specialties*, 36 [4], 45-48, 105-107). An improved synthetic detergent mixture results from the use of 30 to 70% sodium sulfate and $Na_2H_5-xP_3O_{10}$ (where $x=4$ or 5, and the molar ratio of sodium sulfate to the phosphate is 2:1 or 3:1) permitted to co-crystallize to form a complex (Blinka and Henjum, *U.S. 2,941,948*).

The various chemical types of optical brighteners were described, and their differences in substantivity, fastness, and product compatibility were pointed out. Variations in behavior with formulation variation were discussed (Villaume and Allan, *Soap, Perfumery, Cosmetics*, 32, 892-896, 914). Properties, methods of application, and reactions of the fluorescent optical brighteners were discussed (Adams, *Indian Oil & Soap J.*, 3, 56-73). Compatibility between optical brighteners and chemical bleaches in the same composition could be solved by use of chlorine-stable brighteners; need exists for brighteners adapted to a wider range of fibers (Ferris, *Soap Chem. Specialties*, 35 [9], 79-81, 126-127).

Improved lathering properties of detergent compositions could be achieved with N-tris(methylol)methyl fatty amides (Schramm, *U.S. 2,927,081*) while the properties of fatty monoethanolamides for this purpose were reviewed (Anon., *Soap, Perfumery, Cosmetics*, 32, 1246-1248); intensification of perfume and good emollient character are indicated as other effects of their addition.

A broad-spectrum bacteriostat and fungicide, tetrachlorosalicylanilide, was noted as useful for many products, chemically stable, and substantive to many fibers (Lennon, Furia, and Zussman, *Soap Chem. Specialties*, 36 [3], 51-54, 93; [4], 56-58, 109). A 99% reduction in bacteria numbers can be achieved in laundering bedding if it is machine-washed with water above 145°F., 10- to 20-min. wash cycle, and if an effective germicide is put in the rinse (Foter, *Soap Chem. Specialties*, 36 [4], 73-76, 103; [5], 127-133, 139-141).

Soap antioxidants and causes of rancidity were discussed; sodium hydrosulfite, sodium sulfoxylate, thiosulfates, thiosulfites, and many other agents (Anon., *Mfg. Chemist*, 30, 324). The light stability of soaps containing phenolic antiseptics, such as thiobis(chlorophenol) can be prevented from darkening by including an ultraviolet absorber, such as isobutyl p-amino benzoate and sodium sulfite (Kleyn, *U.S. 2,921,907*).

Di- and trivalent metal ion chelation by sodium gluconate can improve bottle washing, paint stripping and aluminum cleaning compositions (Downey and McCallion, *Soap Chem. Specialties*, 35 [10], 45-47, 58).

To prevent decomposition by excessive temperatures of hormones, enzymes, and similar biologicals used in soap compositions, addition of silver tetraiodomercurate, which changes color to a definite temperature limit, is used (Lehner, *Ger. 1,002,105*).

Dicyandiamide is said to prevent the discoloration of copper-containing metals when added to compositions containing an organic surfactant and alkali metal polyphosphates normally causing tarnish (Light, *U.S. 2,967,832*). Tarnish of copper-containing alloys by detergent compositions containing polyphosphates can be prevented by inclusion of a water-soluble inorganic and organic stannous salt, such as stannous chloride, fluoride, tartrate, etc. (Ruff and Smith, *U.S. 2,903,431*).

Skin irritation of alkylbenzene sulfonates or higher alkylphenyl ethers of polyethylene glycol may be reduced by the addition of at least 0.1% by weight of N-lauroylsarcosine or its water-soluble salts (Dvorkovitz, Berst, and Leist, *U.S. 2,962,448*).

Addition of formamide to compositions containing reactive oxygen (e.g., perborates) increases the rate of oxygen release at temperatures below the bath boiling point (Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler, *Ger. 1,010,048*).

Compositions

ALKYLARYL SULFONATES. The following compositions contain effective amounts of alkylaryl sulfonates though other classifications, such as liquids may also contain them. One composition comprised 10 to 40 weight % surfactant and 60 to 90 detergent builder; the surfactant was a mixture of normal primary C_{10} to C_{15} monoalkylbenzene sulfonate 5 to 50, branched chain C_8 to C_{15} monoalkylbenzene sulfonate 35 to 90, and 2 to 15 weight % C_{11} to C_{18} saturated primary monohydric alcohols, and C_{14} to C_{22} 1,2-glycols (Lew, *U.S. 2,956,025*). The organic active ingredient mixture of another composition comprised branched-chain C_8 to C_{15} monoalkylbenzene sulfonate

40 to 50; C₁₄ to C₁₈ primary saturated monohydric alcohols and C₁₄ to C₂₂ alkane 1,2-glycols 5 to 10; 10 to 50 weight % of normal alkane sulfonate or the α -carboxy, β -sulfo, β -hydroxy, or β -nitro substituted derivatives of these alkanes (Lew, *U.S. 2,956,026*). A composition is revealed that is a mixture of alkylaryl sulfonates of C₈ to C₁₄ alkyl groups, and N-alkyl β -aminopropionates (Freese and Witteoff, *U.S. 2,929,788*). An emulsifier consists of the cyclohexylammonium salt of an alkylbenzene sulfonic acid containing at least one alkyl group of at least 3 carbon atoms and a nonionic alkylphenol (C₈ to C₁₅ in the alkylated portion) and 7 to 30 oxyethylene groups (Hyatt, Mayhew, and Nunn, *U.S. 2,946,721*). A foam-controlled detergent consisted of a ternary combination of alkylbenzene sulfonate (molecular weight, 242-250), pentamer benzene sulfonate (molecular weight, 260-310), and an inorganic polyphosphate (Vitale, Bruns, and Leonard, *U.S. 2,949,425*). A suds-enhanced detergent contains as active ingredient a combination of a C₁₂ polypropylene benzene sulfonate and a straight-chain C₁₈ to C₁₈ straight-chain alkylbenzene sulfonate (Stayner, *U.S. 2,944,028*). Detergents of stable and persistent foam were produced by mixtures of C₈ to C₁₅ monoalkylbenzene sulfonates, a N-acylaminoalkane sulfonate from hydrogenated tallow fatty acids, and a foam-improving agent, 1 to 5% p-n-dodecylphenol (Stayner and Lew, *U.S. 2,921,030*).

An oil-soluble surfactant consists of an amine salt of an alkylated aromatic sulfonate and a polyether of at least 1,200 molecular weight attributable to oxyalkylene groups 2 to 4 carbon atoms in length (Kirkpatrick and Seale, *U.S. 2,946,747*).

An essentially salt-free alkylaryl sulfonate (C₈ to C₁₅ alkyl chain) is prepared by the dissolving of the sulfonic acid in a hydrocarbon solvent and adding an inorganic base slurry and a nonionic surfactant. The product consists of solvent, surfactant, and the salt of an organic compound from which inorganic sulfate precipitates (Costine and Behrens, *U.S. 2,945,818*).

A foaming detergent consists of 25 to 75 parts by weight of the anionic sulfate of a polyoxyethylene derivative of a compound of at least 10 C, 75 to 0 parts of an alkyl (C₁ to C₂₀) aryl sulfonate, and 10 to 90% of the combined weight of the anionics as a polyoxyethylene nonionic ether of a multibranched primary C₈ to C₁₈ alcohol (Jelinek and Mayhew, *U.S. 2,941,951*). Claimed was the sulfuric reaction product, the molecular structure of which contained a C₈ to C₁₅ alkyl group and 5 to 60% of a fatty acid amide (Wilson, *U.S. 2,965,576*). A laundering composition comprising a sulfuric acid reaction product, the structure of which contains an alkyl radical C₈ to C₁₅ in length, at least an equal weight of alkali metal phosphate, and, as a suds depressant, a mixture of at least three compounds with acyl radicals of different carbon atom content (C₁₆ to C₂₀) and the water-soluble soaps of these acids (St. John and Griebstein, *U.S. 2,954,347*). A suds-depressant mixture contains, in addition to saturated fatty acids, a nonionic polyoxyalkylene compound (Schwoeppe, *U.S. 2,954,348*; see *U.S. 2,954,347*).

A detergent is claimed that comprises an alkyl (C₈ to C₂₀) aryl sulfonate, which, after preliminary removal of spent sulfuric acid by centrifugation, is mixed with 20% of a C₁ to C₁ aliphatic alcohol to react with free sulfuric acid to form a crystallizable sulfate, then precipitated (Pengilly, *Brit. 820,340*).

Claimed is a synergistic mixture of salts of long-chain alkyl sulfates and α -sulfonated fatty acids C₁₆ to C₂₄ in length (made from lard, tallow, grease, and fish oil fatty acids (Stirton, Weil, and Maurer, *U.S. 2,915,473*).

Nonionic detergent mixtures with tripolyphosphate and other builders can be made with the reaction product of 10 to 20 mols of ethylene oxide with 1 mol of a glyceryl-1,3-dialkyl ether (Blake, *U.S. 2,932,616*).

Perborate-containing alkylaryl sulfonate detergent mixtures are stabilized and have enhanced bleaching action when soluble copper salts are included (Food Machinery and Chemical Corporation, *Brit. 819,842*).

NONIONICS. A nonionic surfactant is produced by the synergistic effect of a mixture of a tall oil fatty alkylolamide and a tridecyl polyoxyethylene ether (Weeks, *U.S. 2,913,417*). A solid cake of a nonionic composition is formed by fusing with an alkyl (C₈ to C₆) phenyl-8 to 10 oxyethylene adduct, the tetrahydrate of calcium nitrate, and urea (Shiraeff, *U.S. 2,927,900*). About 2 to 50% of a N-urea glucoside monofatty ester is mixed with water-soluble phosphates, alkali metal sulfates, and sodium carboxymethyl cellulose to give an improved nonionic detergent (Osipow and York, *U.S. 2,921,909*).

MISCELLANEOUS. A grease-removal composition, particularly effective because of the synergistic relationship between fatty acid and neutral salts in the presence of soap and water to promote grease solubilization, and contains an organic solvent, with or without added alcohol (Spring, *U.S. 2,901,433*).

An oil-in-water cleaning emulsion consists of 0.1 to 5% by weight of a dimethylpolysiloxane, 0.5 to 50% water-miscible or-

ganic solvent for the polysiloxane, 0.01 to 1% nonionic or anionic water-soluble surfactant and water (Terry, *U.S. 2,955,047*).

Corrosive action of sequestrant aminopolycarboxylic acids and salts on aluminum, zinc, and German silver can be inhibited by the addition of monoalkyl polyethyleneglycol phosphates, where the alkyl chain is 14 to 22 C and the glycol is preferably the di-, tri-, or tetra-ethylene compound (McCune, *U.S. 2,921,908*).

Soap tablets are prepared with a nonhygroscopic, readily water-soluble, film-forming substance with an added agent to improve the wettability of the soap (Kapee Chemische Fab. G.m.b.H., *Brit. 823,118*).

A wax-like product formed by combining roughly equal parts of a quaternary with soap is said to be useful in oils in cosmetics and as an emulsifier aid. Nonionic solubilizers may also be used to improve the effectiveness of the composition (Heald, *Am. Perfumer Aromat.*, 75 [4], 45-47).

An abrasive porcelain cleaner consists of a major proportion of silica and up to about 20% of a water-soluble surfactant (Diaz, *U.S. 2,945,815*).

A penetrant composition contains 50 to 95% water, 0.5 to 5% sodium alkylaryl sulfonate, 3 to 35% of an alkanolamine with at least 2 C per molecule, an alkanolammonium hydroxide with 8 to 12 C, or an ammonium salt of a hydroxy carboxylic acid C₁ to C₁₅ in length (Salisbury and White, *U.S. 2,951,039*).

A nonaqueous defoaming composition consists of 45 to 95% of an oil in which is dispersed 0.5 to 10% water-insoluble metallic soap, 0.5 to 10% of secondary amines with an alkyl group derived from mixed fatty acids, and 1 to 10% of a completely esterified polyoxyalkylene polyhydric alcohol fatty acid ester (Lam, *U.S. 2,956,971*).

The bluing action of soap, anionic, or nonionic detergents is improved by an agent called "CI Acid Blue T/321" (Gebhardt, *U.S. 2,930,760*).

A dry-cleaning composition consists of 93 to 99.75 weight % of a volatile dry-cleaning liquid and 0.25 to 7% of a detergent composition. The detergent is 70 to 95% of a hydroxyl organic compound of C₈ to C₁₅ in length, condensed with 2 to 8 mols of 2 to 3 C alkylene oxide, combined with 3 to 30% of the alkaline salt of the sulfate of the condensation product (Lewis and Weeks, *U.S. 2,941,952*).

LIQUID COMPOSITIONS. A light-duty, liquid composition with no phase separation between 40 and 80°F. can be prepared from 10 to 25% sodium dodecylbenzene sulfonate, 1 to 5% fatty acid monoethanolamide (acid C₁₀ to C₁₁), 2 to 10% potassium pyrophosphate, 10 to 12% urea, 5 to 10% ethanol, and from 1.5 to 4% citric acid; the balance is water and pH adjusted to 5 to 7 (Coskie, *Brit. 815,851*). A liquid, clear between 40 to 80°F., was comprised of 10 to 25% sodium dodecylbenzene sulfonate, 1 to 5% fatty acid monoethanolamide (fatty acid C₁₀ to C₁₁), 2 to 10% potassium pyrophosphate, 10 to 12% urea, 5 to 10% ethanol, 1.5 to 4% citric, tartaric, or salicylic acid, and 34 to 70.5% water; the pH was adjusted at 5 to 7 (Coskie, *U.S. 2,947,702*). A composition characterized by liquid clarity up to 100°C. and capable of forming clear solutions in hard water was composed of 7 to 8% sodium dodecylbenzene sulfonate; 24 to 25% alkylbenzene polyether ethanol; 5% diethanolamide mixture (72% diethanolamide, 1% diethanolamine laurate, 21% diethanolamine, 6% glycerol); 3% hexylene glycol; 3% ethanol; 0.1% tetrasodium ethylene diamine tetra-acetate; water to make 100% (Cook, *U.S. 2,943,058*). A concentrated, stable liquid was composed of 25 to 40% of the sulfate of an alcohol (C₁₀ to C₁₆) condensed with 1 to 5 mols ethylene oxide; 6 to 12% of an alkylolamide comprising saturated C_{10,12,14} fatty acids and an alkylolamine; 15 to 25% of ethanol, normal- or iso-propyl alcohol; not more than 5% of ammonium sulfate or chloride; water to make 100% (Korpi and Davis, *U.S. 2,941,950*). A liquid dishwashing detergent with high cloud-point and little or no foam consists of about 10% of the benzyl ether of octylphenoxy polyoxyethanol containing 16 ethoxy groups, about 15% of a sodium soap of C₁₂ to C₁₅ fatty acids, about 7% tetra-potassium pyrophosphate, and water to make 100% (Fine-man and Gebelein, *U.S. 2,913,416*). A clear, single-phase, concentrated liquid consists of an alkylaryl sulfonate salt, magnesium chloride or sulfate, or calcium chloride to improve foam, solubilized in a mixture of low-molecular-weight alcohol, and water (Grifo, *U.S. 2,908,651*).

For building liquid, heavy-duty detergents the preferred compounds are potassium polyphosphates for their synergistic effect with surfactants, their high solubility, and their stability (Van Wazer and Liss, *Soap Chem. Specialties*, 35[12], 59-61, 144). A stable, free-flowing thixotropic heavy-duty liquid is comprised of a water-soluble surfactant, a polyphosphate in an aqueous alcoholic medium. The amount of salt is in excess of its normal solubility in the amount of water present and maintained in a permanently noncaking suspension in the presence

of minor proportions of a nonsoluble wax, a substantially water-insoluble colloidal material, and a water-soluble nitrogen compound, such as urea or thiourea (Hearn, MacLean, and Trusler, *U.S.* 2,920,045). A heavy-duty liquid that yields a small amount of suds is prepared by combining a nonionic surfactant with appropriate quantities of carboxymethyl cellulose and an alkanolamide (Kopp, *U.S.* 2,914,483). A stable, opaque, mucilaginous, aqueous liquid, which does not separate into two or more layers, consists of 10 to 22% sodium dodecylbenzene sulfonate, 15 to 22% potassium pyrophosphate, 2 to 5% fatty acid monoethanolamide, 3 to 5% ethanol, and 3 to 5% glycerol or 1 to 3% propylene glycol (Pengilly, *Brit.* 815,850).

Potassium liquid soaps are made noncorrosive to copper and copper-base alloys by the addition of 2-mercaptobenzothiazole or an alkali metal salt thereof (Golub and Sylvester, *U.S.* 2,912,385).

A shampoo and conditioning composition consists of a) a major proportion of an ampholytic surfactant or its mixture with an equal weight of nonionic surfactant, and b) a minor proportion of a cationic surfactant with an equimolar amount of an anionic, nonsoap surfactant. The ratio of a) to b) should be from 2:1 to 20:1 by weight (Goff, *U.S.* 2,950,255). A hair conditioner and shampoo as a clear liquid consists of 10 to 35% of a fatty acid monoglyceride sulfate, 7% of *N*(lauryl colamino formylmethyl) pyridinium chloride, and an aqueous alcoholic medium (Anderson, *U.S.* 2,928,772).

A clear, homogeneous liquid for paint cleaning consists of 9 to 2 parts by volume of a normally liquid hydrocarbon, 1 to 3 parts of an organic phosphate ester, 2 parts of a monoalkylether of a polymethylene glycol containing 2 to 4 methylene groups, 1 to 5 parts hydrophilic nonionic surfactant, and 1 to 5 parts of a lipophilic nonionic surfactant (Blank, *U.S.* 2,951,043).

GERMICIDAL COMPOSITIONS. A germicidal soap containing thiuram sulfide, with each thiuram nitrogen atom fully substituted with aliphatic groups, contains as a stabilizer a stannous compound or a compound of group IVA element below silicon and in a valence state of more than 2 (Goldwasser, *U.S.* 2,927,899). Zinc carbonate and/or zinc phosphate acts as a light stabilizer and has increased germicidal range and effectiveness when used in soaps containing halogenated hydroxydiphenyl compounds, halogenated (or nonhalogenated) salicylic acid anilides, and thiuram compounds (Farbenfabriken Bayer A.-G., *Brit.* 817,130). Tri-halogenated (like or unlike halogen) tris-phenols, and their mono-alkali metal salts exhibit antiseptic action in soap compositions when present in minor proportions (Beaver, Stoffel, and Shumard, *U.S.* 2,026,141).

A soap or surfactant composition with unusual lasting characteristics consists of 0.1 to 10 weight % of a germicide which is a synergistic mixture of 65 to 98% 3,5,4'-trihalosalicylanilide and 35 to 2% of 5,4'-dihalosalicylanilide (Stecker, *U.S.* 2,906,711). Soap or anionic surfactant compositions with a comparatively high activity against gram-positive organisms also has unexpectedly high activity against gram-negative bacteria owing to the increased solubility of dichloro-*m*-xylenol (Maurice, *U.S.* 2,906,664).

Some of the halogenated bisphenols show antibacterial synergism when combined with some halogenated aromatic anilides and carbanilides by *in vitro* tests. The most active synergism, regardless of the surfactant carrier (or water), took place with hexachloro- and tetrachloro-compounds, the trichlorocarbanilides, and the chlorinated salicylanilides (Noel, Casely, Linfield, and Harriman, *Appl. Microbiol.*, 8, 1-4).

A disinfectant composition comprised water, a disinfecting amount of dichlorobenzyl alcohol, an alcohol solvent, and an anionic surfactant (Schraufstatter, Gottsacker, and Wolz, *U.S.* 2,945,782).

A widely effective skin germicide consists of a combination of polyoxyethylene alkyl phenol, an anionic sulfate or sulfonate, and a calcium sequestrant, such as ethylene diamine tetra-acetic acid or its salts (Davis and Grand, *U.S.* 2,904,468).

ANALYSIS

New cation-exchange resins (Lewalit CN 206), based on polyacrylic acid, were successful in separating cationic from nonionic surfactants and can be used to separate some anionics from nonionics (Hempel and Kirschnek, *Fette, Seifen, und Anstrichmittel*, 61, 369-374).

The nature of the hydrophobic groups and of the alkylene oxide chain-length for nonionic surfactants may be obtained by titrating their ethanol solutions with water to a turbidity end-point. Details of the procedure are given. The method is said also to be useful for alkylbenzenes and hydrocarbons (Kaertkemeyer, *Ind. chim. belge Suppl.*, 2, 538-542). Anionic and cationic surfactant equivalent weights may be determined

by passing warm solutions through Zeo-Karb 225(H) ion exchange resin, followed by titration with standard sodium hydroxide solution (Russell and Whitaker, *Analyst*, 84, 253-254).

The *p*-toluidine and benzidine methods for analysis of anionic surfactants were improved by back-titrating with standard sodium nitrite instead of sodium hydroxide (Nemoto, *Yukagaku*, 9, 65-69). The *p*-toluidine method was used for the analysis of secondary alkyl sulfate salts (Getmanskii, *Masloboino Zhirovaya Prom.*, 25 [7], 29-31). When anionic surfactants were estimated by butanol extraction, the Epton and Weatherburn methods gave lower values. Other attempts were made at improvement of the methylene blue back-titration procedure (Izawa and Kimura, *Yukagaku*, 9, 69-72, 124-128, 296-299).

Alkylarenesulfonates may be determined by photometric turbidimetry; titrating is done with a dilute solution of cationic surfactant to the equivalence point. Interferences by organic solvents, nonionic surfactants, and inorganic solvents are noted (Wiekbold, *Seifen-Öle-Fette-Wachse*, 85, 415-416).

Anionic surfactants were chromatographed on paper after removing inorganic salts by filtration from ethanol solution, treatment with cation exchange resin, and acid hydrolysis. Pinaeryptol Yellow was used as the coloring agent, with several developing solvents. *R_f* values for a variety of surfactants were given (Yamamoto, Shimamoto, and Kobayashi, *Kōgyō Kagaku Zasshi*, 62, 1549-1551).

Infrared spectra for sodium and calcium stearates and palmitates were compared among α -, β -, and γ -forms of the sodium salts and the mono- and anhydrate forms of the calcium salts in the 4000-650 cm^{-1} range (Kewano, *Nippon Kagaku Zasshi*, 81, 1805-1808). Infrared examination of alkyl sulfates and sulfonates and alkylaryl sulfonates requires a salt soluble in the solvents employed. Cyclohexylammonium salts were found acceptable. Spectral features at several levels were noted, and structural interpretations were given (LaLau and Dahmen, *Spectrochim. Acta* 1957, *Suppl.*, 594-600).

With the increasing importance of polyoxyalkylene surfactants, considerable analytical effort has been expended on these materials. Precipitation with various alkaloid precipitating reagents and organic base-precipitating agents was investigated. Bismuth nitrate plus KI was a good precipitant as were heteropolyphosphates, bismuth nitrate plus KSCN, and sodium tetraphenylborate (Harada and Kimura, *Yukagaku*, 8, 523-528). Separation of nonionic surfactants from wool waste products was achieved by passing an aqueous ethanolic dispersion through an alumina column and eluting with water. Molybdophosphoric acid precipitation of the eluate was used for nonionic estimation (Hobson and Hartley, *Analyst*, 85, 193-196). The barium phosphotungstic acid complex method was used for nonionic polyalkyl compounds; the composition of the complex was determined gravimetrically (Kimura and Harada, *Fette, Seifen, und Anstrichmittel*, 61, 930-934).

An ascending paper chromatographic method permitted detection of polyethylene glycol in the presence of the nonionic surfactants. Several procedures were described; a semiquantitative spot area method gave rapid estimation to the nearest percentage (Ginn, Church, and Harris, *Anal. Chem.*, 33, 143-145). Described was a simplified, paper-chromatographic method, based upon the minimum detectable amount obtained with water-saturated butanol as the solvent and a modified Dragendorff reagent as the spray reagent. The by-product, polyethylene glycol, was thus approximately determined (Nagayama and Isa, *Yukagaku*, 9, 77-79).

The distribution of the products by alkaline catalysis of the addition of ethylene oxide to lauryl alcohol and nonylphenol were determined by exact distillation. The results conformed better to a Weibull than to the Poisson distribution. Distribution constants were determined according to the Weibull general formula (Nagase and Sakaguchi, *Kōgyō Kagaku Zasshi*, 63, 588-592).

A 103-reference review of the rheology of soaps was prepared (Sekiguchi and Kimura, *Yukagaku*, 9, 399-406).

PHYSICAL CHARACTERISTICS

Detergency

Lawrence (*Nature*, 183, 1491-1494) suggests that detergency results not from free surface-energy phenomena but by cryoscopic forces only. Phase diagrams and microphotographs are used to interpret these soap-water amphiphilic systems. The cryoscopic forces are interpreted as effective in the immediate vicinity of the soil-substrate system. Electron micrographs (Powe, *Tex. Res. J.*, 29, 879-884) of natural soil *in situ* were used to identify and to determine the soil particle size. These suggested that clay mineral 0.01 to 1 μ diameter was the major particulate material contributing to soil build-up on cotton fibers. Chromatograms (Walter, *Melliand Textilber.*, 40, 646-

651) of fresh and stale skin fat demonstrate decrease in unsaturated fatty acid content, increase in unsaponifiable matter, and resinification on aging. Iron enhances resinification. Calcium soaps adsorb skin fat and interfere with the absorption of fluorescent brightening agents. Synthetic detergents containing polymeric phosphates overcome this and, to some extent, iron contamination, also appeared more efficient than soap in removing skin fat.

Redeposition of soil on cotton fabrics and rinsing of detergent from them are substantially influenced by the phase region of the $\text{Ca}^{++}\text{-Na}_2\text{P}_2\text{O}_7$ system, in which washing and rinsing take place. Rinsing of detergent is improved as the triphosphate concentration is increased or as the Ca^{++} concentration is decreased. Redeposition is retarded and rinsing promoted by higher triphosphate concentrations in the wash cycle (Diamond and Grove, *Tex. Res. J.*, 29, 863-872).

Suggested detergent formulation improvements for use with new textile fibers are: improved soil-suspending action; improved brightener action; more versatile formulations useful in cold, warm, or hot water; better emulsifying action; a fiber rinse to reduce static electricity (Borghetty and Gantz, *Soap Chem. Specialties*, 35, [9], 63-65, 199).

The detergent action of surfactants was reviewed (Tachibana, *Yukagaku*, 9, 219).

The degree of flocculation of aqueous suspensions of ferric oxide and carbon was studied as a function of concentration, time, and intensity of agitation. Average floc sizes were determined turbidimetrically, and the average size always increased with increasing concentration and decreasing speed of agitation (Reich and Vold, *J. Phys. Chem.*, 63, 1497-1501).

A redeposition index test method was developed by using clay suspensions in a Terg-O-Tometer. The method was accurate and gave a yield proportional to the amount of soil deposited. Correlation between clay and natural soil at different soil concentrations was good (Martin and Davis, *Soap Chem. Specialties*, 36 [4], 49-51, 109; [5], 73-76, 255).

Dispersing ability of 14 nonionic surfactants of medium (9-14) HLB was excellent for calcium carbonate and similar to that of sodium pyrophosphate. Nonionics with HLB greater than 15 showed little dispersancy for calcium carbonate (Matsumura and Iwasaki, *Kogyō Kagaku Zasshi*, 63, 970-973). Reviewed were the suspending abilities of surfactants in aqueous solution (Meguro and Kondo, *Yukagaku*, 9, 264-267), as were the solid-liquid interface phenomena in nonaqueous systems (Sakurai, *Yukagaku*, 9, 258-263).

Wetting

Ethylene oxide nonionics (10, 20, 30 mols) of nonylphenol, dodecyl- and octadecylalcohols, -amides, and -amines showed higher wetting velocity for the ether and amide types than for the amines. Wetting velocity decreased with increase in ethylene oxide content. An experimental equation was developed: $V_a/V_c = -0.85 \log k + 1.39$ (Nemoto, *Yukagaku*, 8, 35-36).

Conventional hydrocarbon wetting agents were incapable of wetting Teflon and polyethylene, two low-energy solids. As anticipated, solutions of fluorinated aliphatic acids and salts were able to depress the surface tension of water below the critical surface tension of the polymers, and to wet them completely (Bernett and Zisman, *J. Phys. Chem.*, 63, 1911-1916).

Preferential wetting tensions were measured on films of polyvinyl acetate, nitrocellulose, and cellulose acetate in linseed oil and in aqueous solutions of nonionic agent (10-11 molar polyoxyethylene decyl, dodecyl, and hexadecyl ethers). The films, more easily wetted by oil than by water, became more easily wetted by aqueous solutions of the nonionics, more so when the surfactant hydrophobe was smaller (Kuroiwa, *Kogyō Kagaku Zasshi*, 63, 2064-2065).

A review, with 152 references, was made of wetting and contact angle data (Tsunoda and Sasaki, *Yukagaku*, 9, 246-255).

Foam

Strong evidence that a hydrous gel structure makes up the surface film in a soap or detergent foam was derived by surfactant quantity adsorbed at the air/water boundary, coupled with x-ray diffraction measurements. In a tentative model of gel structure, in which the surfactants are readily dispersible, no close packing of the hydrocarbon chains appears. Closely packed surface hydrocarbon chains in a surface film constitute a special case, associated only with very insoluble monolayers spread carefully on the water surface (Dasher and Mabis, *J. Phys. Chem.*, 64, 77-83).

Low-foaming nonionics could be obtained by the introduction of two hydrophobic groups; this prevented close vertical packing of the surface and thereby reduced the intermolecular hydrogen bonding between the surface molecules, thus giving a

weaker film. These surfactants retain good wetting, draining, and other surface-active properties (Dupre, Wolfrom, and Fordyce, *Soap Chem. Specialties*, 36 [2], 55-58, 91-93; [3], 55-56, 112).

Foam was the subject of a 103-reference review (Okazaki and Sasaki, *Yukagaku*, 9, 231-238).

Dodecyl sulfate salts (various ammonium compounds) showed minimum surface tension at higher concentrations of the smaller counter ions. The smaller the counter ion, the higher the foam and the more stable. No effect upon iron oxide dispersion was found (Kondo, Meguro, and Sukigara, *Yukagaku*, 9, 63-65).

A review of counter-ion effect on ionic surfactants was made (Meguro and Kondo, *Yukagaku*, 9, 346-350).

Micelles and Solubilization

X-ray diffraction data were used to determine the orientation of micelles, which were found to be different in the three layers of commercial soaps (Nakaido, *Kogyō Kagaku Zasshi* 62, 1835-1837). The critical micelle concentration (cmc) of higher glycidyl ethers was examined, that of $\text{ROCH}_2\text{CH}(\text{OH})\text{CH}_2\text{N}^+(\text{R}')\text{R}''\text{X}^-$ was similar to that of $\text{RN}^+(\text{R}')\text{X}^-$; in the latter the R contained 2-3 more methylene groups than the former. The jointing of the first, $-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2-$, did not act as a hydrophile group but rather was equivalent to the polymethylene C_2-C_3 group (Kuwamura, *Kogyō Kagaku Zasshi*, 63, 980-983).

Emulsions and solubilization were reviewed (Sata, *Yukagaku*, 9, 244-246).

The cmc of solutions of dodecylpyridinium halides was dependent upon the halogens: 17.4 for chloride, 12.5 for bromide, and 4.5 for iodide in millimoles per liter. The effects of added salts were studied, the counter ions were in the order $\text{I} > \text{Br} > \text{SO}_4 > \text{Cl} > \text{IO}_3$. The effect of added salts on sodium dodecylsulfate was $\text{LiCl} > \text{NaCl} > \text{KCl}$ and for dodecylpyridinium bromide, $\text{KCl} > \text{KBr} > \text{KI}$. (Meguro and Kondo, *Nippon Kagaku Zasshi*, 80, 818-823).

A new method for determination of cmc of nonionic surfactants was developed, based upon the absorption spectra of the colored iodine-micelle complex. The absorption maximum was always 360 μ for different surfactants and different solvents. Agreement was found with other methods for estimation. An isobestic point in the absorption spectra was evidence that dissolved iodine was in equilibrium with iodine in the micelle and that only one type of iodine-micelle complex was present (Ross and Olivier, *J. Phys. Chem.*, 63, 1671-1674). The iodine solubilization technique for estimation of cmc was applied to a variety of commercial polyoxyethylene surfactants. These data confirmed the linear dependence between the log of cmc and the ethylene oxide content. With the exception of sorbitan monolaurate these lines varied only in slope from one alcohol hydrophobe to another, having a common intercept at zero ethylene oxide content (Becher, *J. Phys. Chem.*, 63, 1675-1676).

Experiments on sodium monolaurin sulfate revealed that NaCl reduced the cmc and that dye-titration values were lower than those by conductance. Increase in electrolyte concentration caused the difference almost to disappear. Conductance-concentration curves of ionic surfactants with and without nonionic surfactants showed that mixed micelles formed; hydrogen bonds were the main binding factors (Biswas and Mukherji, *J. Phys. Chem.*, 64, 1-4).

The effect of organic solvents upon the micelle formation of surfactants was reviewed (Kitahara, *Yukagaku*, 9, 169-174).

The ratios of solubility of o-phenylphenol, pentachlorophenol, and p-dimethylaminoazobenzene in a surfactant solution to solubility in a similar solution without surfactant were determined. This relative solubilization varies with solution pH and solute pK, being at a maximum for nonionized solute and at half-maximum when pH is equal to pK. The variation of relative solubilization with pH is that which is predicted from treatment of micelles as a separate phase (Dyer, *J. Colloid Sci.* 14, 640-645).

Reviewed were interactions between surfactants and high-molecular compounds (Isemura, *Yukagaku* 9, 267-271). Interaction between surfactants and dyes (Goto, *Yukagaku*, 9, 271-275) and their interaction with nonionic surfactants (Nemoto and Imai, *Nippon Kagaku Zasshi*, 80, 1286-1290) were reviewed as were the interactions between colors and surfactants (Kondo, *Yukagaku* 8, 181-185).

Surveyed were factors contributing to the interactions of phenols with surfactants and other macromolecules and the accompanying decrease in phenol activity as preservatives. Formation of relatively insoluble complexes is suggested as not only inactivating the preservative but also influencing the emulsifying and suspending properties of the surfactant (Kos-tenbauder, *Am. Perfumer Aromat.*, 75 [1], 28-29, 32-33).

Adsorption and Desorption

Reviewed were the adsorption characteristics of surfactants at solution surfaces and at the interface between solid and liquid (Matsuura, *Yukagaku*, 9, 220-223; Tamaki, *Yukagaku*, 9, 283-288).

Interface differential volumes were measured between mercury and aqueous solutions of sodium octyl-, decyl-, and dodecyl-sulfate containing excess Li, K, Mg, or Al sulfate. The concentration of cations necessary to initiate phase separation in adsorbed layers of decylsulfate ions were in the order $Li > Na > K$. Mg and Al did not cause such separation. Octyl sulfate did not separate while dodecyl sulfate separated easily (Eda, *Nippon Kagaku Zasshi*, 81, 689-692).

Selective adsorptivity at air/aqueous solution interfaces was determined with radio-tagged surfactants by the ratio of counts from the dried samples of collapsed foams to those from solutions, and by the concentration of collapsed foams. S^{35} tagged sodium p-dodecylbenzene sulfonate and C^{14} tagged potassium hexadecanoate were used. The selective adsorptivities of the dodecylbenzene sulfonate to Na dodecyl sulfate, K dodecanoate, and K tetradecanoate were 35-50, 180-280, and 5-6, and that of K hexadecanoate to K dodecanoate and K tetradecanoate were 50-66 and 5-8, respectively. The concentration of detergent in a collapsed foam was six times greater than in a solution of Na dodecyl sulfate. The concentration of radioactive Na p-dodecylbenzene sulfonate in collapsed foams was 125 to 155 times larger than in the original solution in the case of admixture with Na dodecyl sulfate (Shinoda and Mashio, *J. Phys. Chem.*, 64, 54-57).

The critical velocity of adsorption of wetting agents was measured by controlled speed acceleration of the wetted surface above the wetting liquid contact with the surface; the critical velocity showed a breaking off of wetting. Surfactants examined in 2 to 3% gelatin solutions in water were alkenyl (C_{12} - C_{16}) succinic acids with ionogenic groups, and polyglycerides (alkyl chains $> C_{20}$) of alkyl phosphinic acids. Within the homologous series the critical velocity increases up to a maximum and was greatest with polyglycerides. Surface-tension depression of aqueous and gelatin solutions increased with alkyl chain-length (Levi and Smirnov, *Kolloid Zhur.*, 21, 315-321).

Monomolecular and cumulative layers were reviewed with 73 references (Matsuura, *Yukagaku*, 9, 224-231).

The adsorption isotherm of radio-labelled ethylene oxide-propylene oxide condensate on standard quartz powder was developed; the high specific activity of the surfactant permitted equilibrium measurements as low as 1 p.p.m. The extent of adsorption was less than that of other nonionic surfactants tested on the same quartz sample (Heydegger and Dunning, *J. Phys. Chem.*, 63, 1613-1615).

The adsorption isotherms for the cation and anion of cetyl-trimethylammonium bromide were measured on kieran cotton, viscose rayon, viscose rayon monofil, and oxycellulose. In the concentration ranges studied, cation exchange and ion-pair adsorptions took place; the former was dependent upon the exchange capacity of the substrate. Ion-pair adsorption began to be important near cmc and also upon the cation-exchange capacity of the substrate. In the presence of electrolyte an additional ion-pair adsorption seemed to occur (Sexsmith and White, *J. Colloid Sci.*, 14, 598-618). By reaction of ethylene oxide with viscose rayon and oxycellulose to minimize changes in accessibility of the carboxy groups, the ion-pair hypothesis of Sexsmith and White was tested. The marked decrease in ion-pair adsorption found after esterification agreed with the hypothesis that the clustering process was dependent upon the presence of exchanged cations to act as nuclei (Gotshal, Rebenfeld, White, *J. Colloid Sci.*, 14, 619-629). A theoretical model was proposed to account for the results obtained when cationic surfactants were adsorbed by cellulose. Factors leading to adsorption maxima were discussed, as were those for anionic surfactants (Sexsmith and White, *J. Colloid Sci.*, 14, 630-639).

Measurements of surface pressure and calculation of molecular weight of surfactant from the two-dimensional gas law were valid if the measurements were made at sufficiently low surface concentrations and when the rate of desorption was decreased by the presence of sufficient electrolyte in the substrate (Rosano and Karg, *J. Phys. Chem.*, 63, 1692-1695). The equilibrium-spreading pressure (π_w) of the oil solutions of surfactants on aqueous substrates can be measured easily and rapidly; it is useful to determine the type and concentration of surfactant in the oil phase. Surface-active acids, bases, salts, and nonionizable substances are easily distinguished by the pH dependence of π_w . Measurements of π_w of the supernatant oil can be used to measure surface areas of solids and heats of adsorption thereon (Fowkes, Ronay, and Schick, *J. Phys. Chem.*, 63, 1684-1686).

Sodium lauryl sulfate and, to a lesser extent, sodium dodecylbenzene sulfonate applied topically to guinea pigs under the conditions of a two-stage multiple application test provoked eczematous action of nickel sulfate and its deep penetration into the skin. Soap at 8% concentration does not elicit the nickel response, nor do Igepon A, Igepon T, two nonionics, and one cationic surfactant (Vinson and Choman, *J. Soc. Cosmetic Chemists*, 11, 127-137).

The activation energy of adsorption of Na dodecylbenzene sulfonate on wool was almost similar to that of dyeing with C.I. Acid Orange 7, both at the acidity of acetic acid. The activation energy of adsorption of the surfactant on wool was much higher at neutrality than at acidity (Nemoto, *Yukagaku*, 9, 65-69).

S^{35} tagged Na dodecylbenzene sulfonate gave an adsorption isotherm on clean cotton of low magnitude, without inflection at cmc. The influence of detergent concentration, particulate soil, detergent adjuncts, and water hardness was also determined. The interaction of P^{32} -labelled $Na_3P_2O_7$ with soiled cotton cloth in the wash solution was studied, and the polyphosphate builder mechanism was discussed. The amount of polyphosphate adsorbed was negligible (Jayson, *J. Appl. Chem. [London]*, 9, 422-435).

Viscosity Character

Nonionic surfactants of stearyl and cetyl alcohols and 10 mols ethylene oxide had cloud-points of 67 and 76°C., respectively, and curves of intrinsic viscosity versus temperature had a maximum at a slightly lower temperature than the cloud-points in each case (Kuroiwa, *Kōgyō Kagaku Zasshi*, 63, 1235-1238). Maximum visco-elasticities took place at about 60% concentration for 30 to 80% solutions of dodecylpolyoxyethylene (4, 7, 12 mols) ether, and nonylphenylpolyoxyethylene (5, 8.5, 17 mols) ether (Kuroiwa, *Kōgyō Kagaku Zasshi*, 63, 1384-1387). The visco-elasticities in the 10 to 60°C. range for the nonylphenyl ether were much lower at temperatures above 20°C. The viscosity at 30% concentration was higher with the adduct of fewer ethylene oxide mols while the reverse was true at 60% or higher concentration (Kuroiwa, *Kōgyō Kagaku Zasshi*, 63, 2065-2067).

Two breaks in the aqueous soap viscosity curves occur at the first and second cmc points. When pure Na oleate was used, a third break in the curve, intermediate between the other two, was shown. This "middle critical concentration" can be accurately determined from the minimum of the concentration curves at a given specific viscosity.

Ethanol, butanol, iso-amyl alcohol, ethylene glycol, and glycerol lower the middle critical concentration, if applied in small amounts, and the water-soluble ones, if applied in large amounts, raise it (Kucher, Storozh, and Yurzhenko, *Dopoviđi Akad. Nauk Ukr.R.S.R.*, 1959 [1], 60-63).

Appearance

The incipient state of saponification of saturated C_6 to C_{15} acids and oleic acid was observed when with nebulizer films were sprayed with dilute NaOH; observations were made under the electron microscope. The finest fibrils of C_{11} - C_{15} acids were about 200 Å wide and 58 Å deep, while soaps of C_{12} and C_{10} acids were about 100 Å wide and 58 Å deep. Drying of Na myristate $\cdot 4H_2O$ and Na caprate $\cdot 3H_2O$ took some time and gave twisted orientation of the molecules (Ogino, *Yukagaku*, 8, 68-72). Use of the same technique with pure stearic and myristic acids but with different solvents and saponifiers gave varying results. Ethanol gave finer and denser fibrils than did water. Lower crystallization took place with sodium carbonate than with NaOH; stearate was fragmentary and myristate linear. Crystallizability decreased in the order $Na > K > NH_4$ soaps (Ogino, *Yukagaku*, 8, 197-201).

Pharmacology

Fatty alcohol sulfates and alkylaryl sulfonates irritate the eyes of rabbits. Fatty acid-protein condensates do not cause irritation over the same concentration ranges; if combined, they can be used to reduce the irritation of the other two (Meinecke, *Fette, Seifen, und Anstrichmittel*, 62, 107-112).

A test was devised to determine substance penetration of the epidermis. Soap solutions accelerated intracutaneous "Quaddel resorption," syndets affected it only slightly, and ointments retarded the effect. These experiments form a basis to influence the degree of water concentration in the extracellular region of the binding tissue (Weber, *Fette, Seifen, und Anstrichmittel* 62, 105-107).

Soap solutions swell hair more than water alone. The stage of maximum swelling, reached in from 2 to 5 min., is dependent upon soap anions. The degree of swelling of anionic

surfactants lies between those of water and soap solutions (Habicht, *Fette, Seifen, und Anstrichmittel*, 61, 985-989). Softening of hair was determined by resistance to cutting and determination of the work necessary to cut the hair. Cutting resistance is temperature-dependent. By use of the second method, softening was established as a function of concentration and fatty acid composition of the soap (Habicht, *Fette, Seifen, und Anstrichmittel*, 62, 101-105). A test for harshness of surfactants depends upon the dissolution of keratin in solutions of given surfactant concentration. Solubilization of 40% keratin by 5% surfactant solution was suggested as the maximum acceptable (Cianetti and Felici, *Rass. chim.*, 10, [1], 7-9).

A lipo-protein detergent for the skin was claimed to acidify the skin, have high buffer action, possess medium detergency, fix amino acids or short peptides on the epidermis or keratin fiber. Comparison is made between this product and other detergent products (Morelle, *Perfumery Essent. Oil Record*, 50, 959-965).

Corrosion

Ten anionic surfactants and triethanolamine were evaluated for corrosive action on four metals. Soft steel was not corroded by sodium oleate, triethanolamine oleate, Turkey red oil, and triethanolamine. Zinc was corroded by every material tested. Tin was corroded only by triethanolamine dodecylbenzene sulfonate and Turkey red oil (Kato and Sato, *Kōgyō Kagaku Zasshi*, 63, 1726-1729). Several amphoteric surfactants were tested for corrosive effects on soft steel, zinc, and aluminum (Kata and Sato, *Kōgyō Kagaku Zasshi* 63, 1739-1742). The corrosive effect of detergents on zinc was studied; the calcium in hard water served to counteract this effect. Protective substances were silicates; mildly corrosive were chlorides and chlorites; inert were sulfates, carbonates, and orthophosphates; polymeric phosphates and perborates were actively corrosive; active-ingredient materials had little corrosive action (Stüpel, *Soap, Perfumery, Cosmetics*, 32, 1111-1118).

Miscellaneous

The properties and performance characteristics of dodecyl and higher-molecular-weight alkylbenzenes were described (Steward, *Soap Chem. Specialties*, 36 [12], 57-60, 154-157). Structure and detergency of surfactants were reviewed (Hayashi, *Yukagaku*, 9, 457-460). Reviews of Japanese studies were made (Tamamushi, *Yukagaku*, 9, 219). The properties of dodecyl- and hexadecylmercaptan condensed with various molar proportions of ethylene oxide were described; the 10- to 20-molar polyoxyethylene dodecylthioether were found better than the others (Nagata, Nemoto, Imai, and Morikawa, *Yukagaku*, 9, 30-33).

Commercial ampholytes are of two types: long-chain N-substituted amino acids and long-chain betaines. The various physical and chemical properties of the first two types are described. Because the betaines are internal quaternary ammonium compounds, it is suggested they be called Intronium surfactants (Moore, *J. Soc. Cosmetic Chemists*, 11, 13-25).

The solution state of surfactants was reviewed (Nakagaki, *Yukagaku*, 9, 238-243).

Special transitions of soap in the presence of water were found at 50°, 70°, and 90°C. Heat treatment affects the ability of water-insoluble soap to swell without affecting its degree of solubility. Insoluble amorphous soap forms thick, consistent, visco-elastic bubbles. These effects appear independent of heat treatment duration (Dervichian, *Soap, Perfumery, Cosmetics*, 10, 1061-1068).

The effects of surfactants upon lubrication were reviewed (Tamai, *Yukagaku*, 8, 2-7).

Cotton yarns impregnated with air-borne soil, a ground soil, and a lignin derivative were exposed to a carbon arc light source, and photodegradative effects were measured by fluidity and breaking-strength tests. No effect upon breaking strength was found, and only air-borne soil caused fluidity changes to indicate photosensitization (Morris and Wilsey, *Textile Res. J.*, 29, 971-974).

Low sulfonated lignin in the sulfur dioxide-hydro-tropic cooking of black liquor was precipitated by cationic surfactants. Precipitating ability was in the order of trimethylalkylammonium chloride < dimethylbenzylalkylammonium chloride < C₁₇H₃₅NH₂CH₂COOH. Alkyl chain-length size (C₁₂-C₁₈) had no effect upon precipitation (Yamamoto, Asaoka, and Suzuki, *Kōgyō Kagaku Zasshi*, 62, 1600-1602).

A quantitative study of the hydration of polyglycol ethers by viscosity measurements was made. Stages of hydration and heats of mixing were followed calorimetrically. Stable monohydrates were discussed in detail. It was hypothesized that molecules of water were taken up by the polyether chain to

form inclusion compounds. Water solubility is explained by the existence of a tetrahydrate form of the polyglycol ether (Boehmke and Hersch, *Fette, Seifen und Anstrichmittel*, 62, 87-91).

The effect of surfactants upon the drainage and physical strength of sulfite pulp was determined. All surfactants that were used facilitated water removal from the sheet, and physical-strength properties were affected. Cationics had the greatest effect, and nonionics acted the same as cationics, but the effects were not as great. Anionic surfactants increased breaking strength and decreased burst and tear. These various effects were believed attributable to the relationship between the electric charge between the surfactants and the pulp fibers (Touchette and Jenness, *Tappi*, 43, 484-489).

Polymerization of vinyl acetate was accelerated in the presence of alkylbenzene sulfonates but retarded in the presence of cationic and nonionic agents. No polymerization took place in the presence of alkyl phosphates. The polymerize in the presence of alkyl pyridinium chloride was assumed to be a branched structure. All agents other than alkyl phosphates accelerated the polymerization of styrene (Bito and Yamakita, *Yukagaku*, 8, 22-27).

Surface activity and surface electrical phenomena were reviewed (Tamamushi and Eda, *Yukagaku*, 9, 255-258).

PERFORMANCE AND USE TESTING

A method for evaluating hard-surface cleaners was said to be simple, reproducible, sensitive to the detection of minor formula changes, and correlatable with actual household usage (Liss and Hilton, *Soap Chem. Specialties*, 36, [8], 51-54).

The *in vitro* effectiveness of deodorant bars can be measured by the Price Serial Basin wash procedure. An alternative method is regression analysis of the log of the final count on the initial count and calculation of percentage reduction from the regression line for a standard initial count representing the population mean. A realistic evaluation on small groups regardless of initial count level is said to result (Travers, Rohloff, Ambye, and Vinson, *J. Soc. Cosmetic Chemists*, 10, 410-412).

The use of radioisotopes in detergent and cosmetic research was reviewed (Nelson, *J. Soc. Cosmetic Chemists*, 10, 320-332).

Sodium alkylarene sulfonates for use as standard substances in detergent chemistry were synthesized and characterized. Straight-chain alkyl benzenes from C₆ to C₁₄, as well as a branched-chain α -dimethyldecylbenzene sulfonate were synthesized. These were characterized by paper chromatography and methylene blue titration. Various R_f values were tabulated (Laws and Hancock, *Nature*, 183, 1473-1474).

The problems in water supplies and purification systems, induced by synthetic detergent composition usage, were reviewed (Cohen, *Soap Chem. Specialties*, 35 [9], 53-56, 119, 121). The fifth annual report of the Association of American Soap and Glycerine Products indicated the advances made in understanding and correcting the effects of surfactants upon water and purification systems (Justice, *Soap Chem. Specialties*, 36 [7], 55-57, 174).

Interest in dry-cleaning technology continues as indicated by a paper on specifications for performance characteristics of such detergents for factors affecting their usage (Schapiro, *Soap Chem. Specialties*, 36 [5], 71-72, 259-260). Laboratory methods were given for the evaluation of dry-cleaning detergents covering detergent stability, solvent solubility, soiled wool detergency, carbon soil redeposition, and water-soluble soil removal. These tests were recommended for screen-testing surfactants and formulations in product development and for comparative evaluation of proprietary compositions (Weeks and Lewis, *Soap Chem. Specialties*, 36[9], 65-68; 36[10], 50, 105-107). An excellent summary was given of the micellar properties of surfactants in the dry-cleaning bath, and the solubilization of water and sodium chloride (Hirsehorn, *Soap Chem. Specialties*, 36[7], 51-54; [8], 62-64, 105-109).

A comprehensive review and some experimental data were given to show the correlation between critical micelle concentration, solubilization, and washing properties of a variety of surfactants. A direct relationship exists between solubilization capacity and activity as an emulsifying agent. Maximum soil removal takes place only when critical concentration has been considerably exceeded (Demchenko, *Masloboino-Zhirovaya Prom.*, 25[7], 36-39). An unique method for imparting a positive electrostatic charge to both fabric and soil to permit soil separation and dispersion involved the usage of named proportions of an organic onium compound, a lower alkanolic acid, and an additive such as aluminum salts of lower alkanolic acids, lower alkoxy celluloses, or polyalkylene oxide waxes (Kling and Lange, *U.S. 2,950,253*).

Yellowing and odor formation in personal garments was attributed to skin fats high in lime soaps. Iron contamination also increases color formation. Tetrasodium pyrophosphate in sufficient amount and dependent upon the detergent will alleviate this condition. Aging of garments (and skin fat) contaminated with iron salts makes cleaning harder and tends to set the yellow stain (Walter, *Melliand Textilber.*, 40, 646-651).

A comparison of various detergents and washing machines was performed with the indication that not all detergents operated equally as well in all machines (Ehrenkranz, *Soap Chem. Specialties*, 36[6], 47-50). Controlled laboratory tests, practical evaluation under laboratory conditions, and consumer evaluation in the field were used in evaluating detergents and in controlling micro-organism contamination (Justice, *Soap Chem. Specialties*, 36[3], 47-50, 93; [4], 54-55).

A new method of evaluating detergency was devised in which dust-treated cotton fabric was immersed in aqueous solutions of high polymers (starch, methylcellulose, and many others), then washed with water or detergent solution (Matsukawa, *Kogyō Kagaku Zasshi*, 62, 1584-1588, 1892-1897).

MISCELLANEOUS

Reviewed were the industrial uses of surfactants, said to be growing at a rate faster than for household detergents (Price, *Soap Chem. Specialties*, 35[12], 55-58, 135-139; Speel, *Soap Chem. Specialties*, 36[9], 59-61, 115). Various types of household surfactants were discussed (Snell and Snell, *Soap Chem. Specialties*, 36[9], 55-58). Comparisons of anionic and nonionic surfactants were made (Renard, *Parfums, cosmet., savons*, 2, 357-365), and recent developments were indicated (Price, *Soap Chem. Specialties*, 36[7], 47-50, 105-107). The history and development of surfactants was reviewed (Subba Rao, *Indian Oil & Soap J.*, 25, 167-174). The biochemical and pharmacological aspects of surfactant usage in food processing were discussed (Aylward, *Chem. & Ind.* [London], 1959, 524-530). Hasegawa discussed drugs and surfactants in Japan (*Yukagaku*, 9, 113-119) while Komori (*Yukagaku*, 9, 428-440) surveyed the Japanese literature on fats and oils for 1959.

A complete list of surfactants in use in this country was developed by McCutcheon (*Soap Chem. Specialties*, 36[10], 53-62). A list of oil-soluble dialkyl sulfosuccinates and their use in pesticides and pharmaceuticals was discussed (Stanley, *Mfg. Chemist*, 31, 242-244).

Emulsions of the oil-in-water class may be broken by using demulsifying agents, such as the ester of a polycarboxy acid and a high-molal nonionic surfactant of a molecular weight range of one to 10,000 (Monson and Jenkins, *U.S.* 2,944,978). An emulsion type of pigmented metal-drawing compound may be made by using soap and gel-forming agents, such as bentonite, carboxymethyl cellulose, etc. A sanitary paper containing emulsified lanolin is obtained by use of a cationic emulsifier, such as a quaternary ammonium, quaternary sulfonium salts or bases, long-chain amine salts, or tertiary sulfonium bases (Yang, *U.S.* 2,944,931). The stability of vinyl emulsions, regardless of monomer, was increased with nonionic surfactants with higher values of hydrophile-lipophile balance (Miura, *Yukagaku*, 9, 73-76).

A water-repellent finish for textiles may be prepared from a fatty acid methylolamide and an anionic surfactant as dispersant (Groves and Roberts, *U.S.* 2,944,921). A quick-breaking skin-cleaning water-in-oil emulsion consisted of 20-70% water; 25-70% liquid paraffinic hydrocarbon solvent; <10% nonionic hydrophilic surfactant; ca. 10% polar organic solvent, such as alcohols, ketones, nitroparaffins, or fatty acids; ca. 2% organophilic quaternary ammonium clay complex (Gianladis, *U.S.* 2,948,686). The role of surfactants in cosmetic emulsions and in typical formulations was discussed (Picktall, *Perfumery Essent. Oil Record*, 51, 299-303).

Sorbitan monopalmitate, used in combination with a weak organic acid, sucrose, and beeswax, prevented hardening of the epilating agent (Brunner, *U.S.* 2,954,324).

A wire-drawing lubricating composition was composed essentially of mineral oil, lard oil, glyceryl monolaurate, oil-soluble alkali metal petroleum sulfonate, and ethylene glycol monobutyl ether (Milberger and Kinneman, *U.S.* 2,948,681).

Products (Excepting Detergents)

EDIBLE, PHARMACEUTICAL, AND COSMETIC FAT PRODUCTS. The 1960 Short Course on Edible Fats conducted by the American Oil Chemists' Society comprised the following lectures that were published in the October and November issues of the Society's *Journal*: fats in human nutrition (Kummerow, *J. Am. Oil Chemists' Soc.*, 37, 503); the use of fats in feeds (Wilder, *ibid.*, 37, 510); refining, bleaching, stabilization, deodorization,

and plasticization of fats, oils, shortening (Rini, *ibid.*, 37, 512); hydrogenation (Allen, *ibid.*, 37, 521); emulsifiers (Brokaw, *ibid.*, 37, 523); production of specialty edible fats (Feuge, *ibid.*, 37, 527); the food and drug laws as viewed by regulatory agencies (Kirk, *ibid.*, 37, 533); problems posed to the food industry by the Food Additives Amendment of 1958 (Robbins, *ibid.*, 37, 535); morphology of fats, oils, and shortenings (Hoerr, *ibid.*, 37, 539); the glyceride structure of fats and oils (Vander Wal, *ibid.*, 37, 595); interesterification of edible fats (Braun, *ibid.*, 37, 598); dietary fat and heart disease (Rathmann, *ibid.*, 37, 601); a nutritive evaluation of over-heated fats (Rice, *et al.*, *ibid.*, 37, 607); newer analytical methods for the fat and oil industry (Mehlenbacher, *ibid.*, 37, 613); economics of world supply of edible fats and oil (Hieronymus, *ibid.*, 37, 617); economic and social factors affecting changes in world-wide usage of fats and oils (Knight, *ibid.*, 37, 622); the art of speculation (McHale, *ibid.*, 37, 629).

Various studies were reported relating to the composition, flavor, stability, and synthesis of milk products. In an investigation of the fatty acids and glycerides of cow's milk fat it was concluded that milk fats contain a variety of individual fatty acids ranging in carbon chain-length from 4 to 26 and of various degrees of unsaturation from monoenes to pentaenes. The unsaturated acids exist in many positional and geometrical isomeric forms. The composition of milk fats is influenced by diet and by the plane of nutrition of the animal (Jaek, *J. Agr. Food Chem.*, 8, 377-380). The physicochemical properties of high-melting and low-melting fractions of milk fats were investigated. Results on various glyceride fractions of milk fat showed that the melting point and points of solidification decreased and that the index of refraction and iodine numbers increased with the increasing index number of the fractions. The first three fractions consisted primarily of the saturated fatty acid glycerides; the last two consisted of the unsaturated acids. Glyceride composition of milk fat varied; it depended on the cow's nutrition (Olenev, *Izvest. Vysshikh Ucheb. Zavedenii, Pishchevaya Tekhnol.*, 1958 [4], 19-24). Some flavor compounds from stored instant nonfat dry milk were identified (Bassette, *Univ. Microfilms* [Ann Arbor Mich.], L.C. Card Mic 59-1888, 91 pp.; Dissertation Abstr., 20, 267-268). Determination of cholesterol in milk showed that a liter of cow's milk contains about 170 mg. of this sterol of which 119 mg. are found in the cream and 16 mg. in the casein (average content 0.55 mg./g.) (Kayser and Tachkova, *Congr. Soc. Pharm. France*, 9^e, Clermont-Ferrand 1957, 135-138).

The influence of fat and carbohydrates of feeding-stuffs on the composition of the triglycerides of milk was investigated. It was concluded that the quantity of fat in the feed influences the yield of milk fat and its composition. A fat intake equivalent to 40% of the fat in the milk with vegetable fodder did not insure lipogenesis, and the unsaturated fatty acids in the glycerides dropped 28%. Such a low unsaturated acid content has a hardening effect on the butter. An intake of 65% of fat based on the fat in the milk increased fat 0.15%, and unsaturated acids rose to 30.5%. The ratio between saturated non-volatile fatty acids and unsaturated fatty acids was within the limits 1.7-1.8. Rations with a fat content of 80-100% of the fat in the milk raised the unsaturated fatty acid content still higher. Raising sugar ration from 15 to 25% of the digestible organic substance increased the fat yield 8-10%. The content of volatile fatty acids increased 15-20% (Kniga, *Intern. Dairy Congr., Proc. 15th Congr., London*, 1, 218-224). Liquid-partition chromatography, using various solvent systems on paper and in packed columns, together with gas-liquid chromatography, permitted the identification of δ -dodecalactone in the steam distillate from fresh milk fat. Because of its characteristic fruity flavor and odor properties, δ -dodecalactone is considered to be of possible significance in the flavor changes of processed and stored dairy products (Tharp and Patton, *J. Dairy Sci.*, 43, 475-479). The effect of deodorized milk fat on the flavor deterioration of dry whole milk was the subject of a dissertation (Tharp, *Univ. Microfilms* [Ann Arbor, Mich.], L.C. Card Mic 59-5132, 100 pp.; Dissertation Abstr., 20, 1505).

From a study of oxidative changes of flavor in milk it appears that these may be caused by oxidation of the fat phase or the fat-free part of milk. In skim milk the development of the so-called sunlight flavor requires the presence of light, proteins, peptides or amino acids, oxygen, and riboflavin. The usual clear, transparent bottles were compared with brown bottles. When exposed to daylight, sunlight flavor was detected in transparent bottles after 5 min., in brown bottles after 20 min. (Samuelsson, *Svenska Mejeritidn.*, 50, 407-412). Identification of volatile monocarbonyl compounds from autoxidized milk fat was reported. Approximately 63% of the isolated monocarbonyl compounds were n-alkanals and 34% alk-2-enals. The possible origin of the identified compounds, their

role in the oxidized flavor of milk fat, and the relationship of the results of this paper to the findings of other works are discussed (Day and Lillard, *J. Dairy Sci.*, 43, 585-597).

Triglyceride structure of a number of fats was studied by use of the specificity of pancreatic lipase for cleaving the fatty acids esterified on the 1 and 3 positions of the glycerol. A comparison, based on structure and composition of blood triglycerides and milk fat in the same animal, suggests that, if blood triglycerides contribute to milk fat, there either must be a rearrangement of fatty acids on the glycerol or a supplementary synthesis of triglycerides which changes the pattern of fatty acid positioning (McCarthy, Patton, and Evans, *J. Dairy Sci.*, 9, 1196-1201). A synthetic unsaturated fatty acid milk was disclosed. It is exemplified by the following composition: approximately 60-80% water, 5 to 10% whey proteins, 5 to 10% fat, 5 to 10% lactose, and 5 to 10% salts. The fat is in the form of fatty acids containing approximately 48 to 52% of linoleic acid (Otto, U.S. 2,923,628). In the process for modifying powdered milk products the product particles are made easily dispersible in water by being coated with an anhydrous liquid surface-active agent, such as lecithin or oleic acid, in an amount of 0.2 to 4% (Sjollema, U.S. 2,953,458).

In addition to composition studies and tests for butterfat, several papers were published on butterfat deterioration. By the use of 21% potassium hydroxide as isomerization agent, higher absorption values of butter triglycerides were found than with 7-10% potassium hydroxide (Mattsson and Swartling, *Milk Dairy Research [Almarp] Rept.*, 55, 8 pp.). Use of gas chromatography and mass spectroscopy in the analysis of the fatty acids found in butter and margarine was reviewed (Hallgren, Stenhagen, and Ryhage, *Acta Chem. Scand.*, 12, 1351). Isolation and identification of the high-molecular-weight saturated fatty acids of butterfat resulted in the following conclusions. Butterfat contains the normal odd-numbered saturated acids, n-nonadecanoic acid (C₁₉), n-heneicosanoic acid (C₂₁), and n-tricosanoic acids (C₂₃). The presence of the normal even-numbered acids, n-octadecanoic acid (C₁₈), n-docosanoic acid (C₂₂), n-tetracosanoic acid (C₂₄), and n-hexacosanoic acid (C₂₆) is conclusively established. n-Eicosanoic acid (C₂₀), formerly assumed to be present in butterfat, has been isolated and identified by its physical and chemical properties (Hansen, Shorland, and Cooke, *J. Dairy Research*, 26, 190-195). Several methods for the determination of diacetyl in butter were reported (de Man and Brandl, *Neth. Milk Dairy J.*, 13, 199-221). A review of detection of adulteration in butterfat was reported (Holla, *Bombay Technologist*, 9, 16-20). The variation of butterfat physical-chemical constants of butter produced in winter and summer was studied (Purenas and Griniene, *Kauno Politech. Inst. Darbai*, 7, 33-39). The influence of milk phospholipids on autooxidation of butterfat was investigated (Haab, *Milchwissenschaft*, 14, 16-18). The effect of antioxidants in fats or butter was studied (Akerman, *Izvest. Vysshikh Ucheb. Zavedeni, Pishchevaya Tekhnol.*, 1959 [2], 51). Churnings under factory conditions of non-washed salted butter and washed and nonwashed unsalted butter were compared. There was no appreciable difference in grade score of the butters either fresh or after storage for four months. The salted butter maintained a better quality for eight months than the unsalted butters. There was no appreciable difference in the grade scores allotted to the washed and nonwashed, unsalted butters (McDowall, Singleton, and LeHeron, *Australian J. Dairy Technol.*, 14, 125). A stable carotene composition especially adapted for the coloring of butter consists of 1 to 30% by weight of β -carotene, suspended in an edible vegetable oil (preferably corn or peanut) containing a small amount of an edible fatty acid with 16 to 22 carbon atoms. Stearic or palmitic are preferred (Bauernfeind and Bunnell, U.S. 2,916,385).

Analyses were made on 19 samples of margarine and 10 samples of shortening from England, Germany, Norway, and Belgium on fat, moisture, vitamin A, and some characteristics of separated fat and fatty acids (Nakazawa, Niiya, and Yokoyama, *Yukagaku*, 9, 200). Similar analyses were made on 18 samples of margarine, seven samples of shortening, two samples of lard, and three samples of butter from the United States (*ibid.*, 383). Common margarines consumed in Finland were analyzed for unsaturated fatty acid content. The following concentration ranges were found: iodine number 38.1-54.3, oleic acid 21.0-44.6%, linoleic acid 3.7-12.1%, linolenic acid 0.7-3.8% (Lampi, Eikren, and Antila, *Suomen Kemistilehti*, 32B, 14). A review of the determination of vitamin A in margarine included 12 references (Naito, *Vitamin*, 13, 371). Subjective measurements of spreading and hardness of table margarine were carried out (Uzzan and Sambuc, *Rev. Franc. Corps Gras*, 6, 531). Rheological tests of margarines were evaluated for reproducibility and correlation with the ease of spreading.

The tests (micropenetration, cone penetration, extrusion, and resistance to cutting) show good reproducibility. Extrusion is considered best for evaluation of the ease of spreading (Naudet and Sambuc, *Grasas y Aceites*, 10, 20).

The following patents were issued relating to the processing and/or composition of margarine or related products: interesterified mixed glyceryl esters (Barsky and Babayan, U.S. 2,914,546); process for making margarine (Knollenberg and Hahn, U.S. 2,915,401); a highly nutritional margarine (Melnick and Gooding, U.S. 2,921,855); and margarine and method for producing same (Melnick and Luckmann, U.S. 2,955,039).

A small laboratory model, wiped-surface heat-exchanger for chilling and texturing shortenings was described (Royce and Morgan Jr., *J. Am. Oil Chemists' Soc.*, 37, 643). A stable liquid shortening that will produce cakes comparable with those made with all hydrogenated superglycerinated plastic shortening consists of an edible liquid oil containing 1 to 8% of a nonfish oil hydrogenated triglyceride (Linteris, U.S. 2,909,432). A powdered fat composition suitable for use as a topping or shortening consists of a dried emulsion of a fat, such as hydrogenated cottonseed or coconut oil and the partial ester of an edible glycol and a high-molecular-weight, saturated fatty acid (12 to 22 carbon atoms) in a matrix of an edible encapsulating substance, such as casein or sucrose (Cameron *et al.*, U.S. 2,913,342). A natural fat such as palm oil, shea butter, lard, beef tallow, or mutton tallow is fractionally crystallized so as to obtain a liquid fraction with a softening point below 30°C. The liquid is then hydrogenated to give a fat with an iodine value in the range of 50 to 65, a softening point in the range of 30 to 45°C., and a dilatation at 20°C. of not less than 1,200 (Wissebach, U.S. 2,942,984). Hydrogenated cottonseed oil, melting at 40°, is heated with 0.02% antioxidant until molten. Then it is cooled to 35° with agitation. This product is sprayed in a cooling chamber at 5° to obtain a powdered fat (Ohtaki, *Japan*, 6477). Measurement of the quality of lard by acid number, extinction at S47E of a sample treated with alkali according to Wurziger and Lindemann, Lea number, and quotient extinction/Lea number (Qp) was studied in regard to the effect of storage of raw material before rendering, rendering temperature, and time and the effect of frying (Wurziger and Lindemann, *Fleischwirtschaft*, 10, 599). The formation of polarographically reducible substances in autoxidizing lard was investigated (Kuta and Quackebush, *J. Am. Oil Chemists' Soc.*, 37, 148). Because of the different amounts of arachidonic acid in lard and goose fat it was found possible to determine the degree of purity of goose fat and the amount of lard adulterant present (Wurziger, *Fette, Seifen, und Anstrichmittel*, 61, 1046). In a study and statistical evaluation on performance characteristics of shortening it was concluded that to obtain shortening of higher water-absorption, one should increase the level of monoglyceride used in the shortening. Icing volume is adversely affected by higher levels of monoglycerides. It is immaterial whether the monoglyceride has 40-44% or 56-58% α mono content, and the I.V. may range from 56 to 90 without producing significant effects on water absorption, icing volume, or cake results. Tempering and the choice of vegetable fat or rearranged meat fat stocks are of importance (Truax and MacDonald, *J. Am. Oil Chemists' Soc.*, 37, 651). Production, refining, chemical properties, and economics of cottonseed and peanut oils are discussed in connection with vanaspati manufacture (Krishna, *Bombay Technologist*, 8, 67).

Normal treatments of flour with chlorine dioxide alone or containing up to 30% chlorine (3.5 g. per sack) have no effect on the essential fatty acid content of the flour. At the higher levels (35.0 g. per sack) of chlorine dioxide treatment, although little change was observed in the essentially fatty acid content of freshly treated flour, considerable destruction of all unsaturated fatty acid was found in the aged flour (Coppock, Daniels, and Eggitt, *Chem. & Ind.*, 1960, 17). The addition of soybean oil to flour increased the amount of extractable gluten and also the amount of glutenin (Kisaki, *Doshisha Jishidai-gaku*, 8, 79). The stability of lard in pastry was not affected by baking after low-temperature storage. The addition of 0.003% citric acid or propyl gallate to the lard did not extend the Schaal-oven life of the pastry made from it. The addition of 0.01% of either BHA or BHT markedly extended the fat stability of the pastry; a combination of BHA and BHT was even more effective (Weir *et al.*, *Food Research*, 25, 120). The effect of seven silicone oils on yellow cakes prepared with institutional and consumer type of cake mixes was determined. Of the silicones tested, none resulted in serious diminution of cake volume when included in the batter at 0.1 or 1.0 p.p.m. (Stadelman and Bennett, *Food Tech.*, 14, 119). A rapidly wettable and soluble creaming powder, which is readily dispersible in hot liquid, consists of coarse, dry particles contain-

ing in integrated form 15 to 42% of edible fat, lacteal nonfat solids with a calcium-to-phosphorus ratio below 0.85, and added lactose equivalent to between 15 and 65% by weight of the total solids in the final product. More than 62% of the total lactose should be in the *beta* form (Ortman, *U.S.* 2,933,393).

Small semisolid particles (0.0002 to 0.0007 in. in diameter) of saturated edible fats or oils are uniformly dispersed throughout a grain flour having discrete particles from about 0.0029 to 0.0070 in. in diameter. The resulting dusting mixture prevents sticking of baking dough to the baking pan (Becker, *U.S.* 2,949,365). A culinary mix suitable for reconstitution into a batter for baked goods contains a flour, a leavening agent, and a dried emulsion consisting of an edible partial ester of a glycol and a higher fatty acid and a fat encapsulated by a matrix of edible hydrophilic solids, such as a proteinaceous material or a mixture of proteinaceous and carbohydrate materials (Elsesser and Bogyo, *U.S.* 2,954,297).

A review with 74 references was published on chromatography of edible oils and their additives (Terada, *Yukagaku*, 8, 604). The problem of taste reversion of soybean oil was discussed (von Pezold, *Fette, Seifen, und Anstrichmittel*, 61, 1018). Glyceride oils consisting of esters of fatty acids containing 8-24 carbon atoms and normally not adapted for use in mayonnaises and salad oils are made suitable for use by random interesterification with glycerol triesters of acetic, propionic, butyric, or caproic acid or their mixtures (Thomas Hedley and Company Ltd., *Brit.* 816,343). Synthetic olive oils were found to contain at least 50% more solid fatty acids, which were identified as iso-oleic acids. Their determination affords a means of detecting synthetic olive oils (Staub and Widmer, *Mitt. Gebiete Lebensm. und Hyg.*, 50, 77). An indirect method of hot fat cooking was described. The process substantially reduces heat damage to the cooking fat and rate of increase of free fatty acids (Smith Jr., *Food Tech.*, 14, 84). The properties of frying fat related to fat absorption in doughnut frying were studied (Stern and Roth, *Cereal Sci. Today*, 4, 176). High-water-content of fried food materials was found to accelerate the oxidation of frying oil, as evidenced by a more rapid increase in peroxide value (Bito and Yamamoto, *Yukagaku*, 9, 41). Changes in iodine, peroxide, and acid values were studied during deep-fat frying of fish meats and vegetables (Yamamoto, Ono, and Tanaka, *Kaseigaku Zasshi*, 10, 57). Corn chips of lower fat-content and superior flavor and texture are produced by the dehydration of the chips from 50% moisture to 15% moisture in an oven at 675 to 725°F. for a period of 30 seconds. The dehydrated chips are then fried in shortening corn oil or other vegetable oil for a period of 25 to 40 seconds at 370°F. (Kunze, Long Jr., and Olson, *U.S.* 2,916,378).

The glycerides, 2-oleopalmitostearin and 2-oleodistearin, which are important components of confectionery fats, were synthesized, and their melting behavior and dilatometric properties were determined (Landmann, Feuge, and Lovegren, *J. Am. Oil Chemists' Soc.*, 37, 638). Purified cocoa butter is characterized by a slight structural viscosity, even in the absence of suspended particles. As fat crystals form in the cocoa butter, the structural viscosity effect is enhanced (Sterling and Wuhmann, *Food Research*, 25, 460). A critical examination was made of the common methods used for the investigation of cocoa butter and chocolate adulterants (Purr, *Fette, Seifen, und Anstrichmittel*, 61, 675). The presence of iso-oleic acid was used to detect the presence of small amounts of hydrogenated fats in cocoa butter and chocolate fats (Purr, Lück, and Kohn, *Rev. intern. chocolat*, 14, 332). Various fat characteristics that are important for the detection of adulterants in chocolates and other confectioneries were reviewed. A paper chromatographic method was described, based on the conversion of the fats with their corresponding hydroxamic acids and their separation into component acids (Pietschmann, *Fette, Seifen, und Anstrichmittel*, 61, 682). The following patents refer to the protection and composition of hard butters: synthetic hard butter (Barsky, Babayan, and Knafo, *U.S.* 2,924,528); process for producing confectioners' hard butter (Roylance, *U.S.* 2,928,745); manufacture of hard butter (Weiss, *U.S.* 2,936,238); and substitutes for palm kernel or coconut oil stearins and cocoa butter (Crawford and Jaspersen, *Brit.* 816,514). A peanut butter product, which is not subject to oil separation and which has good spreadability over a wide temperature range, was disclosed (Rowland and Williams Jr., *U.S.* 2,911,303). A modification of the method of Hadorn and Jungkuntz was used for the determination of fat in mayonnaise (Diemair and Salvisberg, *Z. Lebensm. Untersuch. und Forsch.*, 110, 366). A mayonnaise-like product of relatively low caloric content was patented (Spitzer et al., *U.S.* 2,944,906).

Other patented food items include: a dry gravy or sauce mix (Keller, 2,909,431); a cheese-like protein (Hirsch, Gibbs, and Hemmings, *U.S.* 2,919,192); a dry food product recon-

stitutable in water to prepare a cheese souffle (Kline and Rogers, *U.S.* 2,939,792); a puffed edible food product, made by heating bacon rinds with bacon grease at pressures of 5 to 20 p.s.i. (O'Brien and O'Brien, *U.S.* 2,907,660); a process for preparing a water-dispersible, alcohol-soluble phosphatide composition (Davis and Iveson, *U.S.* 2,910,362); a method for heading a solid, fusible higher fatty acid ester of glycerine (Kascher, *U.S.* 2,908,041); a mixture convertible into a semi-permanent mass having a density analogous to that of whipped cream containing vegetable gum, acidulated water, sugar, salt, an edible butterfat emulsion, and an edible gas under pressure (Levin, *U.S.* 2,924,530); solid flavoring compositions containing sucrose esters and process of making the same (Schultz and Talburt, *U.S.* 2,929,722); a similar formulation in which the sucrose ester is replaced with lecithin (Schultz and Talburt, *U.S.* 2,929,723); a composition particularly suitable for use as a frozen milk-product mix additive consisting of a commercial glyceryl monostearate and a glyceryl monomyristate, from 3 to 15% on weight of stearate (Miller, *U.S.* 2,935,406); a similar product with glyceryl mono-oleate substituted for the monomyristate (Miller, *U.S.* 2,935,410); a process for manufacturing a fat-containing, dried dairy product characterized by high wettability and dispersibility in cold water (McIntire and Loo, *U.S.* 2,941,886); salts of basic amino acids and linoleic acid (Chang and Moyer, *U.S.* 2,945,049); oily base for liquid foods that is stable, has a pleasant taste, and is soluble in water or in liquid foods (Nakaoka et al., *Japan*, 1959, 3733); the incorporation of small amounts of fatty acids, having at least 12 carbon atoms or their salts, into an instant coffee formulation in order substantially to reduce foaming when the coffee is dissolved in water (Barch and Reich, *U.S.* 2,929,716); an annatto derivative that is dissolved in a hydrocarbon solvent, oleic acid, and an amine, with resulting mixture emulsified in water, maintained at a pH between 7 and 13, and applied to the skin of citrus fruits to dye them (Keller, *U.S.* 2,943,943); a soapstock from soybean oil containing xanthophyll that was refined, dried, and added to poultry feed for skin pigmentation (Kruse and Cravens, *U.S.* 2,924,525); a liquid feed supplement for chicks in the form of an aqueous corn oil (10%) emulsion, suggested as a means of supplying high-level oil diet without the difficulties of mixing and storing oily diets (March and Biely, *Poultry Sci.*, 39, 279).

A review of chemical methods and economics on the development of nonedible fats for edible purposes was prepared (Chakrabarty, Chakrabarty, and Sen, *Indian Soap J.*, 24, 283). Various patents issued on the coating and packaging of food products include: a typical hot-melt coating consisting of ethyl cellulose, a nontoxic plasticizer such as a fatty acid derivative, mineral oil, wax, an epoxidized natural glyceride of unsaturated fatty acids, and an antioxidant (Patten and Kelly, *U.S.* 2,909,434); foods, such as raisins which have surface deposits of sugar, first given a coating with starch, then with a wax plasticized with lecithin or an acetylated glyceride (Watters and Brekke, *U.S.* 2,909,435); a closure for conventional containers that has a structure permitting effective amounts of solid odor-absorbing material to be placed in the closure and held by a perforated liner, such closures being suitable for use with edible products like lecithin, mayonnaise, and salad oil (Tessmer and Wilhelm, *U.S.* 2,915,404); in the treatment of green coffee beans preparatory to roasting, a recommendation that the beans be coated with a solution of coffee bean wax so that the wax penetrates the beans and inhibits perspiration of the beans during roasting (Specht and Specht, *U.S.* 2,917,387); a method of packaging slices of fat-containing meat and cheese for refrigerated storage consisting of dusting a coating of water-swelling cellulose gum powder on the surface of the slice and juxtaposing another slice with its surface upon and in contact with the coated surface (Long, *U.S.* 2,927,029); a transparent, flexible wrapper for fresh meat consisting of a regenerated cellulose film having on one surface from 2 to 4 g. per square meter of a heat-sealable, continuous coating, composed essentially of a film-former, a blending agent, and a moisture-proofing agent (Hoffman, Janosik, and Ten Broeck Jr., *U.S.* 2,931,732); to reduce moisture loss, meat wrapped in an air-permeable, moisture-retarding film of a fatty compound such as ethyl stearate (Anderson, *U.S.* 2,948,623); and finely divided, dry protopectin coated with a hydrophobic composition in an amount of from 4% to not more than 10% of the total weight of the protopectin (Work, *U.S.* 2,952,548).

Whereas articles on fat deterioration are reported in Section E, some publications involving household food items are mentioned here. A review with 68 references appeared on the storage and preservation of fatty foods (Kapur and Srivastava, *Food Sci.*, 8, 257). A distillation method for the quantitative determination of malonaldehyde in rancid foods was reported

(Tarladgis *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 44). Ethyl oleate, olive oil, and lard have been exposed to the action of ultraviolet rays in the presence of air. Peroxide, acid, iodine, and hydroxyl values as well as spectroscopic determination of *trans*-isomerism were employed to follow the course of the reaction (Kühn and Lück, *Fette, Seifen, und Anstrichmittel*, 61, 860). The use of various antioxidants for edible oils, fats, and food-containing fats was investigated (Tollenaar, *Tuszoze i Stodki Piarce*, 2, 273). The ultraviolet spectroscopic changes during the autoxidation of fats from slaughterhouses were described (Mirna, *Fette, Seifen, und Anstrichmittel*, 62, 577).

Dehydrated fatty food emulsions with an inert matrix of carboxymethyl cellulose were used to evaluate the role of proteins, phospholipids, and iron compounds in lipid oxidations under accelerated storage conditions at elevated temperatures (Bishov, Henick, and Koch, *Food Research*, 25, 174). Measurement of rancidity in fishery products by the thiobarbituric acid method was reported (Ryan and Stansby, *Com. Fisheries Rev.*, 21 [1], 21). The spectra of the unsaponifiables from rancid butcher's fat indicated the presence of conjugated double bonds (Mirna, *Fette, Seifen, und Anstrichmittel*, 61, 1163).

New types of fatty substances, such as ointment bases in pharmaceuticals, were discussed (Awe, *Fette, Seifen, und Anstrichmittel*, 61, 978). Effect of pH on the antifungal activity of undecylenic acid and its calcium salt was investigated (Prince, *J. Bacteriol.*, 78, 788). Preparations for oral administration, providing for the release of pharmacologically active materials over a controlled, extended period of time, consist of a multiplicity of small pellets containing the following components: polyvinylpyrrolidone, a water-insoluble agent melting above 45°, and a pharmacologically active ingredient (Hill, *U.S. 2,918,411*). A highly palatable, stable liquid suspension for oral therapeutic use consists of aspirin in coconut oil whose settling point has been reduced below 60°F. by interesterification, ester interchange, and/or acidolysis (Buckwalter, *U.S. 2,916,416*). A solid deodorant tablet for oral use consists of a sweetening agent and a masticatory gum material capable of stimulating the taste buds of the oral cavity, and a nontoxic lipid having a particle size of from about 0.1 μ to about 2.0 μ in an amount sufficient to have substantial deodorant power in the mouth (Scanlan, *U.S. 2,922,747*). Lecithin was dissolved in a lower alkanol containing no more than 10% water. The solution was heated with an anion-exchange resin in a free-base form to remove the depressor factor content of the lecithin (McQuarrie and Andersen, *U.S. 2,931,818*). An oral therapeutic composition in dosage unit form for relief of the symptoms of osteoarthritis in human beings consists of the acetone-insoluble fraction of the phosphatides of corn or maize (0.3 to about 1.0 g. per dosage unit) and a pharmaceutical carrier (Calder, *U.S. 2,935,448*). A compound for lowering high blood cholesterol levels has the formula, $C_6H_5CHR(CH_2)_mCOX$. R is an allyl radical or an alkyl radical having 1 to 7 carbon atoms, m is the integer 0 or 1, and X is an anionic group, such as —OH, —OMe (where Me is a pharmacologically acceptable alkali metal) or —OB (B is the cation of a pharmacologically acceptable organic base) (Cottet and Redel, *U.S. 2,937,117*). A solution of fat-soluble vitamin in a fat having a melting point of about 35° is mixed with an aqueous solution of a heat-coagulable, proteinaceous material. The mixture is heated to about 65–85° and homogenized to form an emulsion. The heated emulsion is then spray-dried to complete the denaturation (Rosenberg, *U.S. 2,937,091*). The long-chain fatty acid esters of vitamin B₆ were disclosed (Kummerow and Sakuragi, *U.S. 2,955,115*).

A stable vitamin A product made from mixed aliphatic esters of synthetic vitamin A₁ and an aliphatic ester of neo-vitamin A₁ suspended in aqueous media was patented (Stieg and Kardys, *U.S. 2,907,696*). Vitamin A aldehyde glyoxalidine of high biological availability and improved oxidative stability for use in fortifying animal feeds is disclosed (Benton Jr., *U.S. 2,907,761*). Vitamin A aldehyde is reacted at room temperature with silver oxide under alkaline conditions to give vitamin A alcohol and vitamin A acid, which is readily converted to the alcohol (Klein, *U.S. 2,970,796*). The preparation of vitamin A acetate from vitamin A aldehyde was disclosed (Grassetti and Klein, *U.S. 2,913,487*), and a buccal tablet containing vitamin A acetate was patented (Wershaw, *U.S. 2,949,401*). A comminuted vitamin E composition was disclosed (Benton Jr. and Anderson, *U.S. 2,940,900*). A patent was issued on the preparation of ethers of vitamin A alcohol (Weisler and Baxter, *U.S. 2,941,009*). A multiple-vitamin composition having an oil-dispersed phase and an aqueous continuous phase was disclosed (Philipps, *U.S. 2,953,496*). A coating material designed to prolong the release of the medicament in the gastro-intestinal tract consists of an intimate mixture of a nontoxic, solid hydroxylated lipid material and a nontoxic, solid cellulose deriva-

tive (Reese, Station, and Swintosky, *U.S. 2,921,883*). For the production of controlled release medicaments a therapeutic material and at least 5% of a metal soap of an 8- to 18-carbon atom fatty acid are subjected to compression sufficient to form a gel in which the therapeutic material is embedded. The gel thus formed is then subdivided into granules (Gaunt, *U.S. 2,928,771*). A clear, nonaqueous solubilized liquid composition for cosmetic, pharmaceutical, and industrial purposes consists of the following: 20 to 50% of an oil containing 24 to 100 carbon atoms, 20 to 50% of a low-molecular-weight aliphatic alcohol having 1 to 3 carbons, and 5 to 20% of a high-molecular-weight fatty alcohol having 12 to 24 carbon atoms (Lubowe, *U.S. 2,942,008*). The preparation of such compounds as monosodium monomethyl N-lauroyl aspartate and monosodium monomethyl N-myristoyl glutamate and their inclusion in dental creams, tooth powders, and mouth washes were described (Jungermann, *U.S. 2,909,535*). A dextran ester of a saturated fatty acid containing 14 to 18 carbon atoms, with an average of about three fatty acid radicals per anhydroglucose unit of the dextran, was disclosed. The dextran ester is insoluble in water and forms a thin, adherent protective film when applied to the skin (Novak and Tyree, *U.S. 2,954,372*). A study of the spreading test of skin fats in the region of the capillitium showed varying values in different age groups (Hopf and Winkler, *Fette, Seifen, und Anstrichmittel*, 61, 974).

EMULSIFIERS. Factors affecting oil particle size in the freezing and thawing of fat emulsions were studied (Singleton, Benerito, and White, *J. Am. Oil Chemists' Soc.*, 37, 88). Some characteristics of the membranes protecting oil emulsions in protein solutions were investigated. Expressed olive juice contains emulsified globules of olive oil. Electron photomicrographs of these globules show a rough membrane protecting them against coalescence. Some features of the membranes, such as the existence of "poles" and deposited microcrystals, are disclosed by the photographs and by electron diffraction patterns. Heavy metals appear to concentrate in the membranes and not in the aqueous medium (Martinez Moreno *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 582). The usefulness of emulsifiers and emulsified oils to reduce cohesion in canned white rice was examined (Ferrer, Kester, and Pence, *Food Tech.*, 14, 102). The following patents involve emulsifiers or emulsions: edible oil emulsions which have improved shelf life (Eagon and Greminger, *U.S. 2,906,626*); hydrogenated lecithin and process for preparing same (Cole, *U.S. 2,907,777*); wax emulsion polishes (Barker, *U.S. 2,908,578*); anti-rust, emulsion-resistant mineral oil composition (Cunningham and Dinsmore, *U.S. 2,908,649*); an oil in water emulsion containing at least 74% of oil (Duin and Schaap, *U.S. 2,919,196*); bright-drying polish emulsions (Koenig, von Rosenberg, and Sapper, *U.S. 2,925,349*); process for preparing solid fat compositions from emulsified aqueous media (Schram, *U.S. 2,931,730*); mixed methyl glucoside-glycerol fatty acid ester emulsifiers (Gibbons and Morrow, *U.S. 2,931,797*); monoglyceride aqueous emulsion and process of preparing it (Bour, *U.S. 2,932,574*); process for manufacturing whipped fatty emulsions (Gorman, Christie, and Kraft, *U.S. 2,937,093*); process for a stable oil suspension (Garman, *U.S. 2,951,014*); phosphatide emulsifying agent and process of preparing it (Moyer, Fancher, and Schurr, *U.S. 2,045,869*); and enhanced phosphatide products (Hennessy and Moshy, *U.S. 2,952,694*).

ESTERS, ACIDS, ALCOHOLS, AND OTHER FAT DERIVATIVES. A review with 33 references on the preparation of glycerides was published under the heading: "Petroleum Chemistry and Synthetic Glycerides" (Wada, *Yukagaku*, 8, 327). Diglycerides of the fat-forming acids yields, on esterification with succinic, adipic, and other short-chain dibasic acids, a potentially useful series of compounds ranging from hard, high-melting waxes to viscous oils which will not crystallize. 1,3-Diolein and 1,3-distearin esters of succinic and adipic esters were prepared, and some of their properties were determined (Feuge and Ward, *J. Am. Oil Chemists' Soc.*, 37, 291). A method was devised for determining the relative esterifiability of the primary and secondary hydroxyl groups of glycerol. Contrary to earlier belief, the primary and secondary hydroxyls are not equally esterifiable. The equilibrium constant favoring esterification of primary over secondary is ca. 2.3 at 200°C. and between 6 and 10 at room temperature (Brandner and Birkmeier, *J. Am. Oil Chemists' Soc.*, 37, 390). Preparation of 1,2-diglycerides in about 25% yield was attained by application of a method previously used for the preparation of 1,3-diglycerides; the reaction of fatty acid with glycidyl ester was utilized (Radlowe, Madrigal, and Slutkin, *J. Am. Oil Chemists' Soc.*, 37, 570).

The content of β -monoglycerides in commercial monoglyceride preparations stored for 1½ to 5 years was found to be in the range of 5 to 9% of the total monoglycerides (Hartman,

J. Sci. Food Agric., 11, 191). A laboratory method for the preparation of kilogram quantities of highly pure acetylated alpha-monoglycerides was described (Gruger Jr., Malins, and Gauglitz Jr., *J. Am. Oil Chemists' Soc.*, 37, 214). 1-Monosorbin was prepared from isopropylidene glycerol and sorbic acid by a partial modification of the E. Fischer procedure (Taufel, Franzke, and Dietze, *Fette, Seifen, und Anstrichmittel*, 62, 592). The product of reaction at 150–300° of castor oil, an organic dicarboxy acid, and a polyoxyalkylene compound with an average molecular weight between 1,700 and 7,500 was disclosed (Kirkpatrick and Walker, *U.S.* 2,925,429). Monoglycerides are obtained by reaction of glycerol with triglyceride oil at temperatures of about 240–250° in the presence of an alkaline catalyst. High yields are obtained if, at completion of the reaction, the mixture is cooled rapidly by addition of glycerol to the mixture and distillation off of glycerol without heat being added. Reversion to higher glycerides and free glycerol is thus prevented (Woods, *U.S.* 2,909,540). An unstable form of a solid, polymorphic, fatty monoglyceride of a saturated fatty acid is subjected to mechanical working to bring about a solid-solid transition to the stable polymorphic form (Balduin, *U.S.* 2,910,491).

An investigation was made of the polymorphism in case of the di- and tetra-esters of pentaerythritols by means of capillary melting-point, heating and cooling curves, and x-ray diffraction techniques. Both groups of the esters show the monotropic polymorphism that is a type very similar to the 1,3-glycerides. They exist in three forms, α , β , and β' , and show an increase in melting points in the same order (Malkin and Gupta, *Fette, Seifen, und Anstrichmittel*, 61, 868). 2,2-Dimethoxypropane was used as a reagent for the preparation of methyl esters of fatty acids (Radin, Hajra, and Akahori, *J. Lipid Research*, 1, 250). The preparation of fatty acid esters by alcoholysis of fats was studied. The effects of time, catalyst type, and temperature on the yield of methyl esters from palm oil was studied; a theoretical amount of alcohol was used (Pore, *Oleagineux*, 15, 13). A dissertation involved catalyst studies of vapor-phase esterification of octyl alcohol and acetic acid (Venkatesham, *Univ. Microfilms* [Ann Arbor, Mich.], L.C. Card Mic 59-2330, 174 pp., Dissertation Abstr., 20, 240). Measurements of the dielectric absorption resulting from molecular rotation in β - and α -phase long-chain esters and ethers were described. The energy barriers ΔE , frequency factors A , entropies of activation ΔS , and free energies of activation ΔF at 20° were tabulated (Meakins, *Trans. Faraday Soc.*, 55, 1694). A carboxylic acid, such as oleic, and an alcohol having at least 6 carbon atoms are reacted in the presence of catalytic amounts of titanium dichloride diacetate. The resulting ester has an exceptionally low acid number and a color as light as the original acid (Bond Jr., *U.S.* 2,910,489). In another patented process a carboxylic acid ester, such as a glycol monoester of a fatty acid, is prepared by the reaction of a carboxylic acid having from 6 to about 24 carbon atoms with an alkalene oxide at temperatures of about 75 to 175° in the presence of an ammonium halide catalyst. Quaternary ammonium catalysts are particularly effective (Malkemus, *U.S.* 2,910,490). The mono-n-dodecyl, tetradecyl, hexadecyl, and octadecyl ethers of mono- to tetraethylene glycol, $R(OCH_2CH_2)_nOH$, were synthesized. In the dodecyl, tetradecyl, and hexadecyl series, freezing-point minima took place at $i=3$. The distribution of products in oxyethylation of tetradecanol followed the equations of Weibull and Nycander, with a distribution constant of 3.0 (Wrigley, Stirton, and Howard Jr., *J. Organic Chem.*, 25, 439). The viscosity behavior of aqueous solutions of polyethylene glycol stearyl ether was investigated (Kuroiwa, *Kogyō Kagaku Zasshi* [Ind. Chem. Sect.], 62, 1588). In a patented process for the preparation of starch ethers, starch is reacted with an epoxide containing an aliphatic chain of at least 12 carbon atoms. This may be an epoxy fatty acid, an epoxy fatty acid amide, or an epoxy aliphatic alcohol (Wolff, *U.S.* 2,923,707).

A method for synthesis of long-chain fatty acids containing more than 11 carbon atoms was described (Bhattacharyya, Chakravarty, and Kumar, *Chem. and Ind.*, 1959, 1352). The separation of mixtures of synthetic fatty acids was disclosed in a Russian patent (Tyutyunnikov, Man'kovskaya, and Al'terman, *U.S.S.R.* 117,330). A German patent discloses the use of metal carbonyls as oxidation catalysts in the preparation of synthetic fatty acids from paraffin (Zschimmer, *Ger.* 1,002,749). A fraction boiling at 240–350° was obtained in the production of low-temperature diesel fuel by carbamide deparaffinization. It consisted of normal hydrocarbons and served as raw material for a study of oxidation to fatty acids. Of a total yield of 76%, C₅–C₆ acids made up 3.4%, C₇–C₈ 15.7%, C₁₀–C₁₆ 24.7%, C₁₇–C₂₀ 16.6%, and residue 15.6%. Acid numbers were, respectively, 476.0, 387.9, 382.5, 208.0, and 25.0. Melting points ranged from –21 to 75° (Levin, *Khim. i Tekhnol. Topliv i Masel*, 4

[5], 33). The Fischer-Tropsch synthesis was applied to convert synthetic soft paraffin to fatty acids with a cobalt catalyst on a laboratory and a pilot-plant scale.

The oxidized paraffin contained 30–50% fatty acids, of which 60–70% was C₁₅–C₂₀ acids suitable for soap manufacture (*Jan Liao Hsueh Pao*, 4, 15). Carbon monoxide at atmospheric pressure adds readily to the double bonds of certain long-chain unsaturated compounds in concentrated sulfuric acid to produce branched carboxylic acids. Unsaturated compounds studied were oleic acid, 10-hendecenoic acid, oleyl alcohol, methyl ricinoleate, and linoleic acid. Reaction mechanisms involving intermediate carbonium and oxocarbonium ions were proposed to account for the products (Roe and Swern, *J. Am. Oil Chemists' Soc.*, 37, 661).

A process for preparing fatty acids consists of the following steps. An olefin is reacted with hydrogen and carbon monoxide in the presence of a metallic hydroformylation reaction catalyst at an elevated temperature and an elevated pressure to obtain a mixture containing an aldehyde with one more carbon atom than the olefin. The catalyst is removed, and the demetalled mixture is hydrogenated to convert the aldehyde to the corresponding alcohol. The alcohol is recovered, and the remainder of the hydrogenated mixture is oxidized with nitric acid to give a mixture comprising an organic layer with fatty acids and a nitric acid layer (Franke, Selwitz, and Whitaker, *U.S.* 2,945,050).

A study was made regarding the influence of the side-chain position on the physical properties of alkanes and saturated fatty acids. Refractive index, density, solidification temperature, surface tension, molar refraction, and parachlor were determined in the case of homologues of straight- and branched-chain paraffins and fatty acids (Hager, *Fette, Seifen, und Anstrichmittel*, 62, 7). The preparation of unsaturated fatty acids from acids obtained in the oxidation of paraffin was described. The processing involved chlorination and dechlorination of the oxidation products (Nicolescu *et al.*, *Analele univ. "C.I. Parhon" Bucuresti, Ser. stiint. nat.*, 1958, [18], 57). The preparation of pure fatty acid methyl esters by countercurrent distribution, using acetonitrile-pentane-hexane as a solvent system, was found to provide a source of fatty acids with unchanged double-bond configuration (Scholfeld, Nowakowska, and Dutton, *J. Am. Oil Chemists' Soc.*, 37, 27).

Oleic acid of 99–100% purity was prepared in 36–43% yield from olive oil. The combination of two urea-adduct separations (at room temperature) and three acid soap crystallizations (at 3°C.) gave an oleic acid of high quality without recourse to fractional distillation or low-temperature solvent crystallization (Rubin and Paisley, *J. Am. Oil Chemists' Soc.*, 37, 300). Petroselinic acid of a grade that is suitable for most laboratory applications was prepared by a single crystallization of the mixed fatty acids of parsley seed oil from 90% ethanol. A product of higher purity was prepared from this acid by application of urea segregation techniques for the removal of saturated materials. On the basis of iodine values, if the absence of other unsaturated materials is assumed, the purities of the two preparations are 96.0 and 99.4% (Fore, Holmes, and Bickford, *J. Am. Oil Chemists' Soc.*, 37, 490). In a study of the configuration and the properties of erucic and brassic acids it was concluded that the rates of hydrogenation and oxidation for erucic acid and its derivatives were higher than for brassic acid and its esters. Saponification rates at 25 and 40° of esters of brassic acid were higher (Bulatova, *Pratsi Odes'k. Derzhav. Univ. im. I.I. Mechnikova, Prirodnichi Nauki*, 148 [3], 145).

A procedure was described for the preparation of oleic, linoleic, and linolenic acids with the help of adsorption chromatography. The method gave satisfactory yields of methyl oleate and linoleates, but a poor yield of methyl linolenate. The examination of the infrared spectra of the isolated acids showed that the all-*cis* form of the native acids was not affected during the isolation process (Franzke, *Fette, Seifen, und Anstrichmittel*, 61, 905). The preparation of 8t,10t-octadecadienoic acid from oleic acid was described. Oleic acid was brominated with N-bromosuccinimide, followed by addition of free bromine to the double bond. Upon debromination of the brominated product with zinc in ethanol and fractionation of the resultant ethyl esters, the fractions containing 74–75% of conjugated dienoic acids were combined. The ethyl esters were hydrolyzed; upon irradiation by ultraviolet light of the fatty acids in petroleum ether (40–60°) in the presence of a trace of iodine, and, upon cooling, 8t,10t-octadecadienoic acid, m.p. 56–56.5°, was obtained in 15–20% yield (Gupta and Kummerow, *J. Am. Oil Chemists' Soc.*, 37, 32). A study was made of the conversion of conjugated *cis-trans* octadecadienoates to the *trans-trans* isomers. It was concluded that the conversion of methyl-conjugated *cis-trans* octadecadienoate to the *trans-trans* isomer

takes place easily in the presence of iodine and light. The isomerization reaches an equilibrium when approximately 71% of the conjugation present is in the *trans-trans* form (Chipault and Hawkins, *J. Am. Oil Chemists' Soc.*, 37, 176). A flexible method has been developed for the synthesis of "skipped" polyenoic acids and is exemplified by the preparation of linoleic, γ -linolenic, arachidonic, and docosa-4:7:10:13:16-pentaenoic acids (Osbond and Wickens, *Chem. and Ind.*, 1959, 1288). On adding a 1% solution of bromine in chloroform to a 1% solution of stercularic acid, stirred at 0°, exactly one equivalent of bromine was taken up. The resulting (liquid) dibromide shows absorption bands, one of which is characteristic of $-\text{CBr}-\text{CBr}-$. Esterification (with diazomethane), followed

by heating under reflux in acetone with sodium iodide, rapidly gave methyl sterculate di-iodide. It was hoped that these iodine atoms would easily be eliminated with regeneration of the cyclopropene system, but no products with absorption at 1007 cm^{-1} or 1869 cm^{-1} were detected (Fawcett and Smith, *Chem. and Ind.*, 1960, 871). Diene-, triene-, tetraene-, pentaene-, and hexaene-conjugated fatty acids, obtained by alkali-isomerization of codliver oil, tung oil, and ethyl α -eleostearate, were irradiated with ultraviolet rays. After three hours of irradiation the conjugated structure was destroyed except for the diene. Compounds derived from the ultraviolet, irradiated fatty acids are not completely known (Kayama and Tsuchiya, *Tohoku J. Agr. Research*, 9, 251). The maximum amount of conjugated dienoic acid in soybean oil isomerized with iron pentacarbonyl catalyst was found to be 30% (Hashimoto and Shiina, *Yukagaku*, 9, 79). Solid fatty acids composed mainly of *trans-trans* conjugated dienoic acid were separated from isomerized methyl linoleate by low-temperature crystallization. The oxidation products of the methyl esters of the solid acids in acetone by KMnO_4 included hexanoic, heptanoic, azelaic, sebacic, and oxalic acids. Thus the solid acids were assumed to contain 9,11- and 10,12-octadecadienoic acids (*ibid.*, 376).

An investigation was reported of the published work and patents in the area of catalytic isomerization and polymerization of plant oils with the aid of SO_2 (Vohwinkel, *Farbe und Lack*, 65, 571). The ozonide of methyl 10-undecenoate was reduced directly to methyl 10-hydroxy decanoate with sodium borohydride. 10-Hydroxy decanoic acid was thus obtained in an over-all yield of nearly 60% by saponification of the ester (Benton and Kiess, *J. Org. Chem.*, 25, 470). Dimorphocolic acid, the chief constituent fatty acid of *Dimorphothecca aurantiaca* seed oil, was characterized as an optically active 9-hydroxy-*trans, trans*-10,12-octadecadienoic acid (Smith *et al.*, *J. Am. Chem. Soc.*, 82, 1417). The mandibular glands of the worker honey bee was shown to contain 10-hydroxy-2-decenoic acid. It was assumed that these glands were the source of the acid in the honey bee worker and the queen bee. The acid was isolated by separation with paper chromatography by use of a reversed phase system (Callow, Johnston, and Simpson, *Experientia* 15, 421). The 10-keto fatty acids with 24, 25, 26, 27, and 28 carbon atoms have not until now been completely described. They have been prepared through the condensation of sebacyl chloride monomethyl esters with *n*-alkyl iodides in the presence of a Cu-Zn reagent (Breusch, Baykut, and Ozeris, *Fette, Seifen, und Anstrichmittel*, 61, 891). In a study of derivatives of naphthalene and fatty acids, α -heptanoylnaphthalene was prepared from the corresponding naphthyl bromide and heptyl nitrile by means of the Grignard reaction (Jorand, *Oleagineux*, 15, 185).

A discussion with 10 references dealt with the purification of glycerol contained in sweet water by ion exchange resins (Nozaki and Ishiwata, *Yukagaku*, 9, 44). The influence of trace impurities on the quality of distilled glycerine during storage was investigated (Goyenberg and Zeyepanska, *Oleagineux*, 14, 585). The quantitative analysis of *n*-alcohols by gas-liquid chromatography was described (Link and Morrisette, *J. Am. Oil Chemists' Soc.*, 37, 668). Analytical separation of fatty alcohols by gas chromatography was performed by using, as packing, firebrick coated with 20% diethylene glycol succinate polymer (Paquot, Lifort, and Pourchez, *Rev. Franc. Corps Gras*, 7, 341). Crude fatty alcohols containing hydrocarbons, ethers, or higher fatty esters may be separated by selective adsorption and elution from activated alumina columns (Cahill Jr., *U.S. 2,913,501*). A method of determination of α -tocopherol was developed (Devyatnin and Solunina, *Med. Prom. S.S.S.R.*, 13 [2], 38). Evidence was presented in favor of ϵ -tocopherol being 2,5,8-trimethyl-2-(4,8,12-trimethyl-3,7,11-trienyl)-chroman-6-ol (Green *et al.*, *Chem. and Ind.*, 1960, 73). From the seed fat of *Psoralea corylifolia* a crystalline sterol identified as stigmasterol has been isolated. The sterol's identity was confirmed by conversion to the acetate and benzoate (Khastgir, Datta Gupta, and Sengupta, *Indian J. Appl. Chem.*,

22, 35). It was concluded that the C-(24) ethyl group of stigmasterol is of the α configuration when it is expressed in Plattner's convention (Tsuda, Hayatsu, and Kishida, *Chem. and Ind.*, 1959, 1411). Articles referring to chromatographic methods for sterols included the following: chromatographic isolation of sitosterol from cottonseed oil (Markman and Umarov, *Uzbek. Khim. Zhur., Akad. Nauk. Uzbek. S.S.S.R.*, 1959 [1], 63); chromatography of sterols (Tamura and Matsu-moto, *Yukagaku*, 8, 610); paper chromatography of sterols (Zotti, Capella, and Jacini, *Fette, Seifen, und Anstrichmittel*, 61, 1114); chromatography of sterols and its application for the detection of animal and vegetable fats admixed with one another (Peereboom and Roos, *Fette, Seifen, und Anstrichmittel*, 62, 91); paper chromatography of steroids (Kabasakalian and Basch, *Anal. Chem.*, 32, 458).

Butyric acid oxidized with potassium permanganate at pH 10 gave acetic acid and acetone; similarly $n\text{-C}_6\text{H}_{13}\text{CO}_2\text{H}$ gave acetic acid and butyric acid; $n\text{-C}_8\text{H}_{17}\text{CO}_2\text{H}$ gave acetic acid, propionic acid, butyric acid, and pentanoic acid. The results indicate that β -oxidation took place (Neunhoeffer and Raths, *J. Prakt. Chem.*, 2 [4], 84). Behavior of fatty acids, as an oxidation by-product, in a medium of oxidizing octadecane was studied with acids labelled with C^{14} in a carboxyl group. It was found that the acids, from the moment of their introduction into the reaction medium, were subjected to oxidizing decarboxylation. The rate of this process, although appreciable in the beginning, becomes negligible with time. This decrease in the reaction rate is attributed to the inhibiting action of the oxidation products and to the decrease in activity of free radicals, which restrict the oxidation of the reaction products. An equation expressing the rate of reaction, involving the constant of free radical concentration and the constant of free radical recombination, is derived (Berezin and Ragimova, *Doklady Akad. Nauk Azerbaidzhan. S.S.S.R.*, 15, 219). Oxidation of ethyl oleate with lead tetra-acetate in glacial acetic acid and benzene gave the reaction products in 70% yield, which were di- and mono-acetate of ethyl 9,10-dihydroxystearate, ethyl 9,10-diacetoxymethylstearate, ethyl 9-acetoxymethyl-10-hydroxystearate, ethyl 9-acetoxy-10-octadecanoate, and ethyl-9-acetoxy-methyl-10-octadecenoate, and small amounts of ethyl azelaic half-aldehyde and nonylaldehyde. This oxidation in benzene gave di- and monopropionate of ethyl 9,10-dihydroxystearate, ethyl monopropionoxyoctadecanoate, nonylaldehyde, and ethyl azelaic half-aldehyde (Matsubara, Wakabayashi, and Nakamitsu, *Kogyō Kagaku Zasshi*, 63, 502). Oxidation of methyl oleate in acetic acid and acetic anhydride with Pb tetra-acetate gave di-acetate and mono-acetate of methyl 9,10-dihydroxystearate, methyl mono-acetoxyoctadecenoic acid, nonylaldehyde in a small amount, and azelaic half-aldehyde in a small amount (Matsubara, Wakabayashi, and Nakamitsu, *Nippon Kagaku Zasshi*, 80, 1195). The reaction of methyl palmitoleate with *tert*-butyl chromate at 30° for 30 hrs. gave myristic, lauric, capric, nonanoic, heptanoic, and azelaic acids. This proves that *tert*-butyl chromate effects β -oxidation and isomerization (Watanabe, *Nippon Kagaku Zasshi*, 80, 1187). Long-chain alkyl hydroperoxides were prepared in a state of purity varying from 92-100% by the alkylation of hydrogen peroxide in basic medium with the corresponding alkyl methanesulfonate (Wawzonek, Klimstra, and Kallio, *J. Organic Chem.*, 25, 621). *Trans-trans* methyl linoleate hydroperoxide was prepared from methyl linoleate, obtained by debromination of tetrabromostearic acid, by oxidation with oxygen in petroleum ether solution (Banks *et al.*, *Nature*, 184, 816).

A procedure was described, demonstrating the formation of four hydroperoxide isomers in the autoxidation of methyl oleate in accordance with the free radical chain-reaction concept of autoxidation. Experimental proof was also given for the location of the hydroperoxide group in the α position relative to the double bond. New methodology has been reported in the use of the Lindlar catalyst for the quantitative estimation of peroxides. The quasi six-membered ring theory of oxidation as applied to the atmospheric oxidation of fats has been shown to have no factual basis (Privett and Nickell, *Fette, Seifen, und Anstrichmittel*, 61, 842). The effect of solvent on the ozonization of methyl oleate and on the reductive decomposition of the ozonolysis products has been studied. The use of a reactive solvent, such as methanol or acetic acid, resulted in isolated product yields of 87%. Carbonyl yields before isolation of product were on the order of 90-92%. The use of a nonreactive solvent, such as ethyl acetate or heptane, resulted in low yield and impure products. The results are explained on the basis of the Criegee zwitter-ion mechanism for ozonization (Pryde *et al.*, *J. Organic Chem.*, 25, 618). Compounds of the nonazelaic acid parts obtained by the ozonization and decomposition of oleic acid, when glacial acetic acid was used as the solvent, were identified. The nonazelaic acid part contained pelargonic

acid, and besides caprylic acid in the amount about $\frac{1}{2}$ of the former acid. The identification was made by gas chromatography (Izumi, *Kōgyō Kagaku Zasshi*, 62, 814). Treatment of capric acid with 50% hydrogen peroxide and concentrated sulfuric acid gave percapric acid. To a chilled mixture of 16.45 g. percapric acid and 2.0 g. capric acid were added, drop by drop, 24.58 g. of methyl oleate, then 0.5 g. of concentrated sulfuric acid; the mixture was heated 10–12 hrs. at 100°. Methyl hydroxycaprostearate, n_D^{20} 1.460, d_4^{20} 0.936, was obtained as a residual oil after it was heated under 1-mm. pressure (Lefort and Sorba, *Bull. soc. chim. France*, 1959, 606).

The volatile decomposition products of palm oil and peanut oil were subjected to gas-liquid chromatography. Two isomeric 2,4-decadienals, possessing the stereo-configurations of 2(*trans*)-4(*cis*) and 2(*trans*)-4(*trans*), were found to be present in the ratio of 28:72 (Hoffmann and Keppler, *Nature*, 185, 310). Polyhydroxy fatty acids were prepared from the corresponding conjugated fatty acids by osmium tetroxide oxidation. These products gave, with aldehydes and ketones, the corresponding substituted 1,3-dioxolane fatty acids. Simple hydroxylated fat aldehydes were prepared from the di-azoketones. If the hydrazide of a polyhydroxy acid is condensed with acetyl acetone, an acetylated 3,5-dimethylpyrazolone results which, when hydrogenolyzed, yields the polyhydroxy fatty aldehyde (Kaufmann and Jansen, *Chem. Ber.*, 92, 2789). The long-chain fatty aldehydes have been separated, as their aldehyde dimethyl acetals, by gas-liquid chromatography (Gray, *J. Chromatography*, 4 [1], 52). A method was described that makes it possible to separate the higher fatty aldehydes from biological material and to analyze them chromatographically. The fatty aldehydes were isolated from brain phosphatides as their dinitrophenylhydrazones and identified as palmit-, stear-, and olealdehydes. The absence of higher unsaturated homologues of the fatty aldehydes was of special interest (Kaufmann and Kirschnek, *Fette, Seifen, und Anstrichmittel*, 61, 1119). The preparation of linolenaldehyde and of mixed aldehydes from highly unsaturated sources, such as menhaden oil via the acyloin condensation, was described. Reduction of the acyloins and subsequent cleavage of the glycols gave over-all yields of 85 to 90% free aldehydes. The intermediates in the synthesis as well as the final products were analyzed in part by the novel method of thin-layer silicic acid chromatography (Ganglitz Jr. and Malins, *J. Am. Oil Chemists' Soc.*, 37, 425). It has been possible to subject fatty aldehydes to paper chromatographic analysis after their conversion to 2,4-dinitrophenylhydrazones. The selection of stationary and mobile phases depends upon the chain length and the degree of unsaturation. The separation of the critical pairs and the estimation of unsaturated aldehydes was done through the formation of mercury salt adducts (Kaufmann and Kirschnek, *Fette, Seifen, und Anstrichmittel*, 61, 750). A method for the separation and identification of aldehyde isomers depends upon the separation of an isomer approximately 90% pure by large-volume, gas-liquid partition chromatography. The separated aldehyde is examined by nuclear magnetic resonance to determine the number of α -hydrogens, CH_2 —, and CH — groups and by infrared spectroscopy to establish the presence or absence of $-(\text{CH}_2)_n-$ or $(\text{CH}_2)_n-$ groups, where n is equal to or greater than 4. Finally the aldehyde is reduced to a hydrocarbon by the Wolff-Kishner reaction, and the hydrocarbon is identified by comparison with API standards by gas-liquid partition chromatography (Matthews, Burow, and Snyder, *Anal. Chem.*, 32, 691). Dihydrocivetone and cyclopentadecanone were obtained from kamlolenic acid, the main constituent of kamala seed oil (Bhattacharyya, Chakravarti, and Nayak, *Chem. and Ind.*, 1960, 588).

The magnitude of the dielectric absorption was investigated for a number of dilute solutions of long-chain ketones and ethers in hydrocarbons (di-*n*-decyl ketone, di-*n*-dodecyl ether, etc.). In each case the dielectric absorption increased with decreased temperature, and the results indicated that the equilibrium positions of the molecules in the crystal lattice are nearly equal in energy (Meakins, *Trans. Faraday Soc.*, 55, 1701). The condensation of phenol with stearone and methylheptadecyl ketone has been studied. The bisphenols and other products thus produced were identified by hydroxyl equivalent, molecular weight, infrared spectra, elemental analysis, and preparation of characteristic derivatives (Morriss, Bechtle, and Byerley, *J. Am. Oil Chemists' Soc.*, 37, 646). The lactones in the synthetic fatty acids from oxidized paraffin fraction, boiling at 360–460°, were determined. Fractional distillation of the lactone concentrate yielded two fractions, one contained γ -lactone 91% and β -lactone 8%, the other mostly γ -lactone (Ladyzhnikova and Sudarikova, *Mastoboino-Zhiravaya Prom.*, 25 [7], 39).

The epoxidation of the *cis* and *trans*-isomers of 6,7-octadecenoic acid with permonophthalic and peracetic acids as well as the preparation of epoxides through chlorohydrin synthesis was reported. Infrared investigations showed that, during epoxidation, these acids or their esters retained their original configurations (Farooq and Osman, *Fette, Seifen, und Anstrichmittel*, 61, 636). Reaction rates were studied of the epoxidation of butyl oleate in the presence of acetic or sulfuric acid with 30–60% H_2O_2 . The reaction constant of butyl oleate with peracetic acid in homogeneous solution in acetic acid was 1.54×10^{-3} mole $^{-1}$ sec $^{-1}$ at 24.5 ± 0.5 (Murai, Akasome, and Murakami, *Kōgyō Kagaku Zasshi*, 63, 803). A laboratory process was developed for the continuous countercurrent preparation of epoxidized oils. This consists of introducing continuously, to a packed column, an unsaturated oil, hydrogen peroxide, and acetic acid, and withdrawing the epoxidized product. Operating variables were investigated, and optimum conditions were predicted (Latourette *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 559). The hydrolysis of butyl 9,10-epoxystearate with unhomogeneous acid catalyst proceeded abruptly from about 20%. The reaction was much accelerated by the addition of emulsifiers, increase in the concentration of acid catalyst, and rise in temperature, but it was retarded by the addition of benzene. The hydrolysis with homogeneous acid catalyst in acetone solution was more speedy (Murai, Akasome, and Nishiyama, *Kōgyō Kagaku Zasshi*, 63, 280). Homogeneous reactions of butyl 9,10-epoxystearate with formic, acetic, and butyric acid were studied. The reaction of epoxy groups with a large excess of organic acids conformed well to pseudopimeric reaction. The reaction rate was in the order formic \geq acetic $>$ butyric acid. As butyl 9,10-epoxystearate was difficultly soluble in formic acid, the experiment was made with dioxane with the solvent. The reaction rate was much influenced by the concentration of formic acid in dioxane (Murai, Akasome, and Murakami, *ibid.*, 283).

A study in the reduction of some long-chain epoxy acids appeared to indicate that the conclusion that the catalytic reduction of 9,10-epoxyoctadecanoic acids results in unidirectional opening of the oxirane ring is proved to be misleading (Juliatti *et al.*, *Chem. and Ind.*, 1960, 874). A patented process of epoxidation involves the use of a cation exchange resin. An ester of an unsaturated, higher fatty acid is mixed with acetic acid, aqueous hydrogen peroxide, and a sulfonic acid cation exchange resin. The mixture is heated to the range of 50 to 100° and maintained at this temperature during the epoxidation (Greenspan and Gall, *U.S. 2,919,283*). Another patent discloses unsubstituted polyglycidyl esters of dimers or trimers of long-chain, ethylenically unsaturated aliphatic hydrocarbon acids (Newey, *U.S. 2,940,986*).

A review with 31 references dealt with the theory of catalytic hydrogenation (Keii, *Yukagaku*, 8, 224). The production of higher fatty alcohols by catalytic hydrogenation was the topic of another review with 30 references (Miyagawa, *ibid.*, 236). Equimolar mixtures of a free fatty acid and an ester were hydrogenated at 180° with Ni-kieselguhr catalyst. In the mixture of erucic acid and methyl oleate, free fatty acids were considerably more rapidly hydrogenated than the esters. In the mixture of linoleic acid and methyl linolenate the ester was more rapidly hydrogenated (Hashimoto and Tsuchiya, *Yukagaku*, 9, 83–87). Linolenic acid was hydrogenated by $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ according to the procedure of Aylward and Rao at 50°, using a mole ratio of 5:1 of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ to acid. It was found that no appreciable amounts of *trans* acid were produced during the hydrogenation. Rao, *J. Sci. Ind. Research (India)*, 18B, 131).

Methods for the synthesis of amino acid derivatives of ethanolanine were described. N-Phthaloylglycylaminoethanol may be prepared in 24% yield by a modification of the Sheehan carbodi-imide synthesis of peptides of hydroxy amino acids (Smith, Althouse, and Shigley, *J. Am. Oil Chemists' Soc.*, 37, 288). Gas-liquid chromatography was applied to the separation of fatty amines, which was carried out with nonpolar substrates on solid supports of Chromosorb and Chromosorb W, which were previously treated with potassium hydroxide to overcome adsorptivity. In this manner well-resolved symmetrical peaks were obtained (Link *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 364). The chain-length of high-molecular-weight, fatty primary amines has been successfully determined by gas chromatography. Columns packed either with silicone grease on sodium chloride or with silicone oil on potassium hydroxide-treated Chromosorb W have been used at high temperatures to give satisfactory resolution and symmetry (Nelson and Mihun, *Chem. and Ind.*, 1960, 663). A British patent was issued on the preparation of amines from fatty acids. The acids are converted to amides by ammonia, then to nitriles by further ammonia and dehydration over activated alumina,

and finally to the amines by hydrogenation over a cobalt-molybdate composition (Armour and Company, *Brit. 815,934*). The preparation of fatty amides was described, involving treatment of glycerides with ammonia and a Friedel-Crafts reaction with NH_2COCl (Kaufmann and Skiba, *Fette, Seifen, und Anstrichmittel*, 59, 340). The nonaqueous system used for preparation of long-chain fatty acid amides of sphingosine and dihydrosphingosine has been successfully extended to the synthesis of several long-chain fatty acid amides of serine and its methyl ester (Weiss, *J. Org. Chem.*, 24, 1367). Amides of α -sulfonated palmitic and stearic acids were prepared by various methods. Solubility and surface-active properties were determined (Weil, Stirton, and Bistline Jr., *J. Am. Oil Chemists' Soc.*, 37, 295). Ozonolysis has been used as the initial reaction for the preparation of polyamides from oleic acid. (Otsuki and Funahashi, *Advances in Chem., Series No. 21*, 205).

A German patent specification disclosed a process for the preparation of adipic acid diamide. Adipic acid, 1460 parts, was melted at 152° , the temperature then was raised to 170° , and a stream of ammonia was introduced for 3 hrs. until the formation of the ammonium salt was complete. The mixture was then heated 4 hrs. at 225° with the distilling of aqueous ammonia; the resulting diamide was removed from the reaction vessel and allowed to solidify to give colorless adipic acid diamide, 1420 parts (Merkel and Palm, *Ger. 1,014,097*). *p*-Chloranilides of saturated fatty acids and oleic acid were prepared by either adding *p*-chloraniline to acid chlorides or reacting *p*-chloraniline with fatty acids in *p*-cymene. The products showed high m.p. and were suitable for identification of fatty acids (Kameoka, *Nippon Kagaku Zasshi*, 81, 950-953).

A British patent specification disclosed novel catalysts for preparing dinitriles from dibasic acids. A solution of 4 g. of ammonium metavanadate was prepared in 200 ml. of water; 37.6 g. of potassium hydroxide was added, and the solution was heated to evolve ammonia. Then 52 g. of 89% phosphoric acid and sufficient water to give 1,000 ml. were added. The pH was adjusted to 1.0-6.0. Silicon dioxide gel (100 g.) was immersed in this solution for 30 min., then dried and heated at 300° for 3 hrs. to produce the desired catalyst (Miwa, Ueno, and Fujibayashi, *Brit. 797,945*). The reaction of N_2O_4 with castor oil was investigated. With stoichiometric amounts of N_2O_4 or the liquid reagent, ONO and NO_2 were added to the double bonds of the glycerides. The saturation was complete. With excess N_2O_4 the glycerides decomposed. The saturated and unsaturated acids were separated by nitration and separation of the nitro products. Reduction of the nitroglycerides yielded NH_2OH , NH_4Cl , and nitrogen-free acids (Vasil'ev and Moskov, *Inst. Tonkoi Khim. Tekhnol. im. M.V. Lomonosova*, 1956, [6], 26).

The rhodonation of oleic acid and elaidic acids and their esters was studied. The rhodonation rates for oleic acid and its esters were much higher than for elaidic acid and its esters. Rates for esters were lower than for acids. Chain-lengthening of alcohol radicals and their branching reduced reaction rates of esters in *cis* forms stronger than in *trans* forms (Zhila, *Prirodnichi Nauki*, 148 [3], 161). A method for the preparation of oleic acid from peanut oil, of 98% purity by means of urea complex formation has been described (Khan, *Oleagineux*, 15, 155). Various proportions of biuret-urea mixtures for the formation of urea fatty acid adducts were investigated. The addition of biuret reduces the yield of the addition compounds, and the crystals are smaller in size. The addition of biuret to urea however results in an increased formation of the adducts in the case of saturated fatty acids (Rigamonti and Riccio, *Fette, Seifen, und Anstrichmittel*, 61, 864). The synthesis was described of 1-glyceryl 2-myoinositol phosphate by an interchange reaction between glycerol 1-iodide 2,3-distearate and a silver 2-(1:3:4:5:6-pentaethyl) myo-inositol phenyl phosphate, followed by the removal of the protecting group (Davies and Malkin, *Chem. and Ind.*, 1959, 1155). The methods of Baer and of Verkade for the preparation of dipalmitoylphosphatidic acid were modified in order to obtain greater yields. The phosphatidic acids from soybean and linseed oils were extracted, and the anti-oxidizing power of the phospholipides was determined (Candela and Jacini, *Olii minerali, grassi e saponi, colori e vernici*, 36, 110). A semi-micro method for the colorimetric determination of the phosphorus content in lipids was reported (Korpaczy, *Fette, Seifen und Anstrichmittel*, 61, 748). A new method was described for the isolation of nearly pure total cerebrosides from the fresh brain. Yields in the various steps were close to the theoretical. The presence of lower homologues in all four classes of rat brain cerebroside acids was discovered (Kishimoto and Radin, *J. Lipid Research*, 1, 72). The addition of dialkyl phosphonates to unsaturated compounds under free radical conditions has been shown to be a general reaction of wide applicability. Addition proceeds smoothly with unsatu-

rated compounds containing a terminal or an isolated double bond, also with a series of vinyl esters (Sasin *et al.*, *J. Am. Chem. Soc.*, 81, 6275). As part of a series of articles on sulfurized oils a publication gave details of manufacturing conditions and application characteristics of sulfurized oils, which are prepared with the aid of S_2Cl_2 and elementary sulfur (Schiemann, Doring, and Vohwinkel, *Fette, Seifen, und Anstrichmittel*, 61, 913). The reaction of divinyl sulfone with α -oleostearic acid has been studied. The reaction product was found to be monomeric, consisting of only one divinyl sulfone and one oleostearic moiety. Contrary to expectations, the adduct contained only two ethylenic linkages rather than three, and the addition product is considered to be a transannular sulfone (Placek and Bieckford, *J. Am. Oil Chemists' Soc.*, 37, 400). The preparation of α -sulfonated pelargonic, stearic, and substituted stearic acids was reported (Weil *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 679). Oleic acid and its esters were thiocyanated more rapidly than the corresponding elaidic acid or its esters (Plisov and Zhila, *Zhur. Obshchei Khim.*, 29, 323). A U.S. patent discloses a process for the preparation of halohydroxy fatty materials. Halohydroxy fatty acids, esters, amides, and alcohols are prepared by passing chlorine or bromine into a reaction vessel containing an unsaturated fatty material, water, and caustic (Robin, *U.S. 2,936,314*).

Progress in the field of vinyl derivatives of fats was reviewed. The survey is divided into three main sections, which concern the preparation of vinyl esters and ethers and their uses (Uzzan, *Rev. Franc. Corps. Gras.*, 7, 135). "Vinyl compounds derived from fats" was the topic of another review with 46 references (Asahara and Mitsuhashi, *Yukagaku*, 8, 339). The molecular weight distributions of several conjugated soybean vinyl ether homopolymers were studied by means of the integral fractionation technique. Polymers having number-average molecular weights of 2,200, 4,800, and 10,000, prepared with stannic chloride as catalyst, as well as a polymer having a molecular weight of 3,400, prepared with boron trifluoride as catalyst, were included in the study. The observed distributions for all the polymers were found to approximate the so-called "most probable" distributions expected theoretically for polymers obtained by simple difunctional polymerization (Teeter, Dorman, and Harris, *J. Am. Oil Chemists' Soc.*, 37, 552). Vinyl stearate was separated from a mixture of vinyl stearate and stearic acid by extraction with a paraffin hydrocarbon solvent having no more than 7 carbon atoms (Buselli and Rutledge, *U.S. 2,949,480*). Fatty acid vinyl esters were copolymerized with acrylonitrile in the presence of benzoyl peroxide and dimethylformamide in N_2 . The copolymers contained about 13 mole % of fatty acid vinyl esters. The molecular weight of copolymers was 57,000-136,000. Fatty acids used were caproic, caprylic, capric, myristic, and palmitic acids (Asahara and Mitsuhashi, *Yukagaku*, 9, 33). The reaction of long-chain fatty acid chlorides with acetylene was reviewed (Kaufmann and Stamm, *Fette, Seifen, und Anstrichmittel*, 59, 946).

A study was made of the effect of storage and heating on ricinoleic acid. When ricinoleic acid is heated or kept at room temperature in an inert atmosphere, the main reaction is the formation of estolides; this reaction is of the second order. Pure ricinoleic acid is very reactive; there is a marked drop in its hydroxy value if it is kept at room temperature for more than a few hours. It must be stored as a solid below 4° . The auto-reactions of ricinoleic acid are intramolecular dehydration, the hydroxyl group reacting with either neighboring hydrogen atom to give a mixture of linoleic acids, and intermolecular dehydration, the hydroxyl group condensing with a free carboxyl group of another molecule to form estolides. The reaction can be repeated, giving long-chain polycondensates (Hawke and Kohll, *J.S. African Chem. Inst.*, 12, 1). Chemical dehydration of ricinoleic acid at 180° in the presence of anhydrous sodium acid sulfate was found to proceed in two stages. The first stage forms short-chain estolides and diethenoid acids together with some enanthal and 10-undecenoic acid. In the second stage, as the hydroxyl value approaches zero, rupture of estolide chains commences, forming further quantities of diethenoid acids, mainly conjugated 9,11-octadecadienoic acid. Chemical dehydration is a first-order reaction with respect to hydroxyl value while estolide formation is second-order with respect to neutralization and hydroxyl values (Hawke and Kohl, *J.S. African Chem. Inst.*, 12, 17).

The rate of dehydration of castor oil was found to increase with the number of acidic groups in the catalyst, the order of increase being: benzene-, phenol-, and naphthalene-monosulfonic < disulfonic < trisulfonic < heteropoly acids. A lower temperature of dehydration (200 - 230°) and a reduction of side reactions took place with increase in reactive groups. The introduction of hydroxyl in 1,3,5-benzenetrifluoroic acid miti-

gated hydrolysis and decomposition of the oil while the naphthalene nucleus decreased the activity of the catalyst. Of the three heteropoly acids studied, phosphomolybdic was the least active (Saraf and Dole, *Indian J. Appl. Chem.*, 22, 1). For their separation and identification, the mixed fatty acids of dehydrated castor oil were acetylated, reacted with maleic anhydride and subsequently hydrogenated. At all three stages the products were subjected to paper chromatographic analysis, and the chromatogram was evaluated quantitatively (Chowdhury, *Fette, Seifen, und Anstrichmittel*, 61, 924). Castor oil was heated 5 hrs. at 800 lbs./sq. in. in a nickel-chromium stainless steel autoclave with the same weight of 50% aqueous sodium hydroxide at $310 \pm 5^\circ$ to give sebacic acid in 44.6% yield and capryl alcohol in 28.2% yield. When 3% cadmium oxide was added in the foregoing reaction for 1 hr., it gave 45.6% sebacic acid and 26.7% capryl alcohol (Chu and Lin, *Chemistry (Taipei)*, 1959, 69). A process for the continuous thermal degradation of ricinoleates to give sebacic and oxydecanoic acids was described (Stein, *U.S. 2,913,490*). Sebacic acid, 2-octanol, and 2-octanone were produced by reacting ricinoleic stock with caustic alkali in the presence of sodium or potassium nitrate in a proportion of approximately 1 to 10% by weight, based on the ricinoleic acid in the stock (Bourgeois, *U.S. 2,935,530*). A method for the recovery of pure myristyl alcohol from a reaction mixture, obtained on treatment of castor oil with caustic alkali, was reported in a British patent (*Société des Produits Chimiques de Bezone, Brit. 822,700*; see *U.S. 2,897,243*).

A study of the Varentrapp reaction was made. The alkali fusion of oleic acid gives rise to palmitic acid, acetic acid, and hydrogen as the products of the reaction. The investigations on Varentrapp's reaction shows that, in polyunsaturated fatty acids, alkali fusion gives rise to as many molecules of acetic acid as the number of double bonds in the reacting acids may be. Linoleic and linolenic acids yield two molecules of acetic acid and myristic acid, and three molecules of acetic and lauric acids, respectively (Roncero, Ayerbe, and Romero, *Fette, Seifen, und Anstrichmittel*, 61, 900). In a patented method for degrading unsaturated fatty acids in which an alkali salt of an unsaturated fatty acid, free from alcoholic hydroxy groups, is heated in the presence of an alkali hydroxide, an improvement involves effecting the heating at a temperature of about 300° in the presence of at least 0.05% catalyst selected from the group consisting of lead, bismuth, thallium, or mixtures, alloys, or compounds of these metals (Stein and Hennig, *U.S. 2,921,084*). Castor oil was heated with nitric acid and with manganese dioxide as the catalyst. By this process about 15% of azelaic acid from castor oil could be obtained (Kawahara, *Nara Gakugei Daigaku Kiyo*, 5, 57).

A patented process involves heating of fatty acids at $220\text{--}330^\circ$ in the presence of specified catalysts until the unsaponifiable content is at least 32% (von Mikusch-Buchberg, *U.S. 2,923,718*). Another patent by the same inventor discloses the preparation of condensation products of acid anhydrides (*U.S. 2,923,719*). In a patented process for the polymerization of unsaturated fatty acids the material is heated in the presence of minor proportions of surface-active crystalline clay mineral and water. Incorporated in the reaction mixture is a catalytic amount of an alkali material capable of reacting with the fatty acids to form soap (Myers, Goebel, and Barrett, *U.S. 2,955,121*). Butyl 9,10-epoxystearate synthesized from butyl oleate was studied for decomposition by being heated at $160\text{--}220^\circ$ (Murai, Akazome, and Nishiyama, *Kogyo Kagaku Zasshi*, 62, 1004). The chemical changes of linseed oil acid ethyl esters during pyrolysis were investigated (Axt, *Nahrung*, 3, 18). In order to examine more fully the manner by which ricinoleic acid undergoes thermal decomposition into heptaldehyde and undecylenic acid, a number of related β -hydroxyolefins were prepared and subjected, for short periods of time in a flow system, to temperatures near 500° . The products formed in each case are readily explained in terms of a six-membered cyclic transition state (Arnold and Smolinsky, *J. Am. Chem. Soc.*, 81, 6443). The residue resulting from the pyrolysis of methyl ricinoleate after exhaustive distillation was found to consist of four principal fractions: a) methyl esters, which represented 70% of the total amount and consisted of diunsaturated, oleic, and ricinoleic acid esters; b) glycerides not alcoholized (20% of total); c) polymeric material (6% of total); and d) unsaponifiables (5% of total) (Naudet and Vezinet, *Rev. Franc. Corps Gras*, 7, 385). Pyrolytic spectra were presented of the C_1 to C_6 hydrocarbon products which were formed by the pyrolysis of olive, hydrogenated olive, and coconut oils. A qualitative and quantitative shifting of the components in the chromatograms with a change of the chemical nature of the oil was apparent (Janak, *Nature*, 185, 684).

The electrochemical synthesis of dicarboxylic acids was investigated. A new method makes it possible to synthesize the diesters of higher dicarboxylic acids from the monoesters of lower dicarboxylic acids. The electrochemical synthesis of diethyl sebacate from monomethyl adipate is carried out by use of platinum electrodes and an electrolyte solution, which consists of equal parts of water and the sodium salt of monomethyl adipate (Fuchs and Moritz, *Fette, Seifen, und Anstrichmittel*, 61, 1124). Simplified chromatographic methods have been developed for the separation and analysis of the C_4 through C_{12} straight-chain dicarboxylic acids (Smith, *Anal. Chem.*, 32, 1301). A rapid method was developed for the quantitative analysis of mixtures of three aliphatic C_{10} dibasic acids and two C_6 monobasic acids by gas chromatography (Bartsch, Miller, and Trent, *Anal. Chem.*, 32, 1101). The lattice energies, infrared spectra, and possible cyclization of some dicarboxylic acids were studied (Davies and Thomas, *Trans. Faraday Soc.*, 56, 185). The known process involving conversion of 1-chloro-4-cyano-2-butene to dicyano-octadiene isomers and further hydrogenation to sebacic acid and 3-ethylsuccinic acid, or further reduction to decamethylenediamine and ethylhexamethylenediamine, was improved by effecting the first stage in the presence of metallic iron, with or without addition of activators, such as nickel, cobalt, etc. (Boffa and Quilico, *Ital. 568,323*). The preparation of *trans,trans-muconic* acid is described in a German patent. Adipic acid esters are chlorinated in the presence of BF_3 or its complex compounds to the corresponding α,α' -dichloroadipic acid esters, and hydrochloric acid is split off in usual manner (Sauer and Tusch, *Ger. 956,602*). α -trichloro- ω -cyanoalkanes are hydrolyzed with sulfuric acid to give aliphatic dicarboxylic acids (Oberrauch, *Ger. 1,021,347*).

Preparation of pure gossypol from dianilino-gossypol was described (Smith, *J. Am. Oil Chemists' Soc.*, 37, 286). The scope of the reaction of Schiff base (anil) formation between gossypol and primary amines has been investigated. Seventeen primary amines of widely varying types were reacted with gossypol, and the anil derivatives were isolated (Alley and Shirley, *Org. Chem.*, 24, 1534). When grain oil, extracted with petroleum ether from sawamillet, *Echinochloa crusgalli*, was allowed to stand with a small amount of acetone, crystals of hexagonal tablets were obtained. This substance, $C_{23}H_{32}O$, had m.p. 278° and $[\alpha]_D^{20} 8.2^\circ$. Ultraviolet and infrared spectra of this compound and its oxide showed the absence of carbonyl and conjugated double bond and the presence of trisubstituted double bond ($-\text{CH}=\text{C}:$) and β -methoxy. This new pentacyclic compound was called sawamilletin (Obara and Abe, *Nippon Kagaku Zasshi*, 80, 677). Sawamilletin was shown to be β -methoxy-isolean-14-ene (*ibid.*, 80, 1487). The structure of sawamilletin given in the preceding reference was verified by synthesis from taraxerol (Abe, *ibid.*, 80, 1491). The range of activities of lipoxidase from lentil was found to overlap that from soya beans Blain, Doherty, and Todd, *Chem. and Ind.*, 1959, 1216).

FATTY MATERIALS USED IN TEXTILE AND PAPER TREATMENT, CORROSION INHIBITORS, DEFOAMERS, WAXES, TALL OIL, POLISHES, TANNING AGENTS, MISCELLANEOUS. A number of patents refer to textile treatment and the preparation of photographic stripping paper and copying paper. Textile materials are impregnated with aqueous solutions or dispersions of stearyl carbamic acid and dried at temperatures above 100° to give water-repellent finishes (Doser, *U. S. 2,906,776*). In order to make wool resistant to felting and shrinking it is immersed in an aqueous bath containing the following ingredients: a) between 0.1 and 1.0 g./liter of a polymerized epoxide compound, such as a carboxylic acid epoxyalkyl ester or an epoxidized unsaturated fatty oil; b) an inert solvent, such as tetrahydrofurfuryl alcohol, dioxane, or acetone; c) an emulsifier, e.g., ethylene oxide addition products of fatty acids with 12 to 18 carbon atoms; d) a chlorine and oxygen-releasing material, such as alkali metal hypochlorites. After 5 to 10 min. the wool is removed from the bath and dried at a temperature of about 70° (Rapp, *U.S. 2,926,064*). A dry, free-flowing fabric softener in powdered form that is dispersible in cold water contains an urea inclusion compound of hydrogenated tallow quaternary ammonium salt and a nonionic wetting agent. The softening agent should be present in from 5 to 20% of the total dry product; the amount of urea should be at least 3.5 times the weight of the softening agent; and the amount of wetting agent should be about 5 to 30% of the softening agent (Sniogowski, *U.S. 2,940,816*). The heat-sensitive layer of a copying paper contains, in intimate association, 1 mol of silver behenate, about 1 mol of behenic acid, and about $\frac{1}{2}$ mol of protocatechuic acid. Silver salts of other organic acids, such as stearic, oleic, lauric,

and hydroxystearate, may also be used (Owen, *U.S. 2,910,377*).

A photographic stripping paper involves a paper support, a superficial coating on one surface, consisting of a Werner complex in which a trivalent nuclear chromium atom is coordinated with a carboxylic acid group with a least 10 carbon atoms, and a gelatin silver halide emulsion layer directly over the superficial coating (Bryce and Griggs, *U.S. 2,925,340*). The transferable coating of transfer sheets for forming thermo-sensitive copies consists of 12.2 parts by weight of fatty grey carnauba wax, 11.9 parts of ceresine wax, 30.7 parts of mineral oil, and 27.7 parts of Strong Red Lake. The coating also includes 17.5 parts by weight of graphite for rendering the red written copy matter sufficiently heat-absorptive to produce a heat pattern in a thermo-sensitive copy sheet when the latter is irradiated with infrared radiation when in contact with the copy matter (Francis and Seaward, *U.S. 2,936,247*).

Several patents refer to corrosion inhibitors. Anti-rust agents are prepared by the reaction of itaconic acid with a diamine containing an aliphatic radical of 8 to 30 carbon atoms (3-''soya''-aminopropylamine) (Halter and McGrath, *U.S. 2,908-711*). Organic acid salts of polymeric fat amines are claimed as exceptionally good corrosion inhibitors. Basic raw materials for the preparation of the polymeric fat amines are fatty acids, such as soybean, linseed, corn, safflower, tall oil, etc. The fatty acids have sufficient double bond functionality to form the polymeric material. The organic acid employed to form salts of the amines should have at least four carbon atoms (Anderson, *U.S. 2,913,305*). A stable, noncorrosive composition of matter consists of a solution of a lower alkanolic acid ester of cellulose in a halogen-containing organic solvent with a hydroxy lower alkyl amine nitrite or a cadmium salt of a water-insoluble fatty acid as stabilizer (Rosenthal, *U.S. 2,927,031*).

Novel defoamers were disclosed in various patents. Fatty acid esters of octakis (2-hydroxypropyl) sucrose in which 1 to 8 of the hydroxyl groups have been esterified are used for surfactants, antifoam agents, plasticizers, thermoplastic water-soluble resins, surface coatings, and modifiers in alkyd or urethane resins (Anderson and Melstad, *U.S. 2,909,681*). A material useful in controlling foam in aqueous adhesive solutions consists of a physical mixture of an ethylene glycol-insoluble alkylene-oxide polymer in combination with a long-chain saturated fatty acid or a polyvalent metal salt of a fatty acid (Stephan, *U.S. 2,914,412*). An antifoam composition consists of the following: fatty acids of more than 11 carbons, 3-11 parts; lecithin, 10 to 30 parts; polar esters of polyhydric alcohols and long-chain fatty acids, 0-9 parts. Sufficient fatty acids must be present in the form of an alkali soap to provide at least 0.25% by weight of the antifoam composition (Jurisch, *U.S. 2,923,687*). The development of foam over aqueous liquids may be controlled by the addition of a small quantity of a glyceride oil to which has been added 0.5 to 10% by weight of rice oil sludge (Szumski and Petty, *U.S. 2,923,688*). A substantially sterol-free mixture of fatty acids, rosin acids, and unsaponifiables is prepared by extraction of tall oil pitch with a liquid, normally gaseous hydrocarbon and removal of the sterols. Incorporation of a small amount of this mixture in media having a tendency to foam excessively significantly suppresses the foam (Steiner *et al.*, *U.S. 2,931,780*).

The definition and classification of waxes was reviewed in a German publication (Ludecke, *Fette, Seifen, und Anstrichmittel*, 61, 999). The chloroform-soluble neutral wax isolated from the leaves of *Picea pungens* (Colorado spruce) was shown to contain sabinic, 14-hydroxytetradecanoic, and juniperic acids with minor amounts of nonsaponifiable substances and n-fatty acids. Infrared spectra of the neutral wax showed no free hydroxyl groups, and it was suggested that the neutral wax was composed mainly of a cyclic polymer of the ω -hydroxy acids and that the seasonal changes in acidity were caused by ring opening or closure (Rudloff, *Can. J. Chem.*, 37, 1038).

Mass spectroscopic and gas-liquid chromatographic analyses of paraffin wax isolated from green tobacco leaf, from the black fermented tobacco of a variety of Argentinian cigarettes, and from the smoke of these cigarettes, indicated that the wax from each was a complex mixture of similar composition. n-Hentriacontane (C_{31}) was the main individual component, but appreciable quantities of the C_{29} and the C_{33} homologues were also present. Relatively high concentrations of the branched isomers of C_{29} - C_{33} alkanes were also found. Analyses of the methyl esters of fatty acids from flue-cured tobacco of a variety of British cigarettes showed the major component to be methyl palmitate, accompanied by some stearate and smaller amounts of other higher and lower homologues. Considerable amounts of C_{18} unsaturated esters were also present with methyl linolenate predominating (Carruthers and Johnstone, *Nature*, 184, 1131).

The wax recovered from the waste material left over after separating the fiber from the leaves of the indigenous plants of the Agave family, commonly known as sisal, can replace carnauba wax in many of its uses. Sisal wax resembles carnauba wax in solvent take-up and in the heat-resistance properties that determine the suitability of a wax for use in the preparation of polishing compositions (Mhaskar, Hinge, and Shah, *Research Ind. [New Delhi]*, 4, 219). The wax of sugar cane was found to have the following constants: melting point 80°, d_{25} 0.965, saponification number 11, iodine number 13.8, nonsaponifiable matter 50% (Torricelli, *Ind. vernice [Milan]*, 11, 8). The extraction and constitution of peat wax was reviewed (Howard and Hamer, *J. Am. Oil Chemists' Soc.*, 37, 478). Ouricuri wax was submitted to chromatographic separation. An estimated composition of the wax (in percentage) is hydrocarbons 1.3, simple esters 23.5, hydroxy-mono-esters 22.4, hydroxy-di-esters 17.2, hydroxy-acidic-poly-esters 5.4, free acids 8.7, free alcohols 3.0, resins 14.8, moisture 1.4, and ash 0.4 (Cole and Brown, *J. Am. Oil Chemists' Soc.*, 37, 359). An investigation showed that the wax acid components of natural and partially-synthetic waxes in organic solvents can be separated and ultimately determined quantitatively by use of the adsorption chromatography technique and suitable anion exchangers. The ion exchange method thus offers a simple and exact procedure for the determination not only of free wax acids but also of the total or combined wax acids in case the mixture was saponified beforehand (Presting and Janicke, *Fette, Seifen, und Anstrichmittel*, 62, 81). A patented wax composition has at least 50% of oxidized polyethylene wax containing between 2 and 7% of combined oxygen, with an acid number between 11 and 20, and an average molecular weight between about 1,000 and 5,000. Also present is between 1 and 10% (on weight of oxidized wax) of a water-insoluble aluminum salt of a saturated, aliphatic monocarboxylic acid with from 8 to 20 carbon atoms. The balance of the composition consists of conventional hot-melt coating adhesives (Rosenbaum, *U.S. 2,943,069*).

A German patent refers to an improvement for manufacturing heat-resistant, anhydrous waxy pastes from mixtures (C_{20} - C_{60}) that were prepared from paraffin hydrocarbons by chlorination, dehydrochlorination, catalytic addition of water gas, hydrogenation, and use of an alkali melt (Kolling and Rappen, *Ger. 1,008,726*). Variations in the composition of wool fat were reviewed regarding acid number and light refraction (Nitschke, *Faserforsch. u. Textiltech.*, 10, 380). The fractionation of the methyl esters of wool wax acids by partitioning between two immiscible solvent layers was described. Three fractions were obtained: a fraction rich in hydroxyl content, a fraction low in hydroxyl content, and a small amount of hard, transparent, highly colored material (Noble, Eisner, and Scanlan, *J. Am. Oil Chemists' Soc.*, 37, 14). Paper chromatographic examination of a steam distillate of wool fat showed the presence of butyric, isovaleric, nonanoic, capric, and laetic acids. The presence or absence of conjugated doubly unsaturated or of triply unsaturated acids could not be confirmed. Ultraviolet spectra indicated that a trace of such acids may be present (Janecke and Senft, *Deut. Apoth.-Ztg.*, 97, 820). Chromatographic methods indicated the presence of the following amino acids in wool fat hydrolyzates: aspartic acid, glycine, glutamic acid, serine, alanine, cystine, α -aminobutyric acid, ornithine (or lysine). Traces of glucose, glycerol, and inositol were found in some samples. A lipo-protein present in the unsaponifiable portion of wool fat would explain these results (*ibid.*, 839). A German patent discloses a novel process for the recovery of wool fat (Evans, Ewers, and Simpson, *Ger. 962,630*). Another German patent refers to the saponification of wool fat with calcium or magnesium hydroxide in the presence of additives that accelerate the saponification (Rossouw and Rudloff, *Ger. 1,001,787*).

The following publications referred to liquid resin and tall oil. The liquid resin of southeast France was found to have the following composition and constants: acid value, 157; saponification value, 168; and iodine value, 85. The resin is composed of 47% resin acids, 25% of free fatty acids, 5.3% of combined fatty acids, and about 10% of unsaponifiable material. The fatty acid fraction has the following composition: 17 to 20% linoleic acid, 14 to 16% oleic acid, and about 6% saturated acids, which are mainly palmitic and myristic acids (Desalbres, Dupaya, and Dubearnes, *Rev. Franc. Corps Gras*, 6, 597).

Crude Japanese tall oil was decolorized by heating with 0.3% zinc chloride, followed by distillation. Tall oil was thermodecomposed with p-toluenesulfonic acid to obtain polymerized resin acids and fatty acids (Waida and Terauchi, *Kogyô Kagaku Zasshi*, 62, 1734). The isolation and identification of trace amounts of the normal odd-numbered fatty acid, n-heptadecanoic (margaric) acid from tall oil, was reported. The

weight of n-heptadecanoic acids that was isolated represents approximately 0.01% of the total weight of the tall oil (Cooke and Hansen, *Chem. and Ind.*, 1959, 1516). A patented process for the preparation of a tall oil suitable for use in reclaiming rubber was described. Heating the crude tall oil at approximately 130° for 24 to 36 hrs., then adding 3.5 to 7.5% of a stabilizing solution prevents crystallization of the abietic acid (Van Valkenburgh, *U.S. 2,908,676*).

A few publications referred to polish compositions containing fats or waxes. The inclusion of a new modified tall oil fatty acid "Indusoil 57-118" in amine soap emulsifier systems for wax dispersions produced dry bright polishes, combining economy with high gloss, superior levelling, and wear properties (Hackett *et al.*, *Soap Chem. Specialties*, 36 [7], 77). The addition of a dialkyl citrate (dioleoyl or distearyl) to a carnauba wax formulation produces a polish which is easily buffed, has high gloss, and has no tendency to chalk (Landwerlen and Vahlteich, *U.S. 2,909,437*). A pressurized polishing composition, in addition to the propellant, contains 10-30% finely divided abrasive; 5-16% wax; 2-12% polydialkylsiloxane; 40-75% hydrocarbon solvent; 1-4% ethylene glycol monoalkyl ether with 1 to 7 carbon atoms in the alkyl group, and 1-10% oleophilic amorphous thickener dispersible in the solvent (Kendall and Meister, *U.S. 2,040,378*).

Several patents disclosed tanning and fat-liquoring compositions. Leathers with improved pliability and water resistance are produced by the impregnation of skins with a synthetic resin, prepared by condensing cyanamide or its derivatives with a high-molecular-weight amine derived from fatty acids of 12 to 22 carbon atoms (Heyden and Plapper, *U.S. 2,913,304*). A fat-liquoring composition for chrome-tanned hides and skins consists of an oil base and about 2 to 20% of a masking agent. This masking agent is a mono-ester or a tri- or tetra-basic acid, in which the alcohol radical contains from 12 to 18 carbon atoms (Plapper, Heyden, and Arnold, *U.S. 2,950,950*). Pongam oil is sulfonated to yield a fat liquor (Radhanandakishore and Nayudamma, *Indian 62*, 348). Sardine fish oil is sulfonated and mixed with fatty oils and/or mineral oils to obtain a fat-liquoring composition in the form of a stable emulsion (Radhanandakishore and Nayudamma, *Indian*, 62, 566).

A miscellaneous group of compositions containing fat derivatives was disclosed in the following patents. Certain compounds are claimed to act both as dispersing agents and as sticking agents in a fungicidal agricultural spray. These compounds are salts of a volatile base (ammonia, tri-ethylamine, etc.) and a long-chain fatty acid, either saturated or containing at least 2 double bonds (Hartley and Park, *U.S. 2,907,691*). The inclusion of 0.25 to about 5% of a polymeric linoleic acid, with a molecular weight of above 300 and from 30 to 60 carbon atoms, in a coal-spraying composition gives improved dust-allaying and weathering properties as well as increased coverage (Neesley, *U.S. 2,913,349*). The addition of a small amount of a salt of morpholine and oleic acid to a hydrocarbon mixture boiling in the gasoline range reduces the stalling tendencies of the motor fuel (Cantrell and Peters, *U.S. 2,920,944*). The addition of a synthetic long straight-chain primary alcohol, containing an odd number of carbon atoms, retards the evaporation of water from a surface (Crawford and Stoops, *U.S. 2,925,318*). A gelled liquid hydrocarbon consists of a liquid hydrocarbon and about 0.5 to 3.0% by weight of a gelling agent. This gelling agent is an alkali metal or ammonium soap of aliphatic, monocarboxylic acids of at least 14 carbons of which at least 10% should contain 20 or more carbon atoms (Steiner and Gibson, *U.S. 2,946,748*).

Products (Excepting Detergents)

DRYING OILS, PAINTS, RESINS, AND PLASTICIZERS. A review on *Nicotiana tabacum* (tobacco) covered the use of tobacco oil as a stand oil and in the manufacture of varnishes, alkyd resins, and inks (Balbi-Olearia, 13, 118). Analytical constants were determined on the oils of *Malva neglecta*, *M. moscheta*, and *M. meluca*, which were classed as drying oils, and on the oil of *M. sylvestris* (Shelud'ko and Goikhman, *Nekotorye Voprosy Farmatsii, Sbornik Nauch. Trudov Vyssh. Farm Ucheb. Zavedeni' Ukr., S.S.S.R.*, 1956, 190) and the seed oil of *Clitoria ternatea* (Tiwari and Gupta, *J. Proc. Oil Technologists Assoc., India, Kanpur 13*[1-2], 9), which were semi-drying oils. Investigation of a large number of vegetable oils in a search for new industrial oils revealed 20 samples which had iodine values above 180. Most of these were from the *Euphorbiaceae* (spurge) and *Labiatae* (mint) families (Earle *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 48, 440). The oil from *Dimorphothea aurantiaca* (cape marigold) contained 50% of a fatty acid containing a hydroxyl group and a conjugated diene structure (Earle *et al.*, *ibid.*, 254).

Studies of the oxidation of fatty acids and their simple derivatives have a bearing on drying oil chemistry because they help to explain the mechanisms by which oils dry. In the autoxidation of unsaturated fatty acids a straight-line relation existed between the logarithms of the time of maximum peroxide content and the temperature, also between the logarithms of the time of maximum rate of peroxide formation and the temperature (Pietrzyk, *Roczniki Technol. i Chem. Zywosci*, 3, 77). The oxidation of linoleic, linolenic, alpha-oleostearic, arachidonic, elupanodonic, and erucic acids in emulsions and as the dry acids in the presence of catalysts (cortisone, cupric ions, and cobalt ions) was studied. Cupric ions had the most pronounced effect (Schuler *et al.*, *Fette, Seifen, und Anstrichmittel*, 62, 389). *trans* Isomers were autoxidized more rapidly than *cis* isomers when thin films of linseed oil methyl esters were exposed to ultraviolet light (Helme *et al.*, *Rev. Franc. Corps Gras*, 6, 609). Sodium chloride did not accelerate the autoxidation of emulsions of methyl linoleate or linoleic acid, as indicated by the rate of oxygen uptake (Mabrouk and Dugan, *J. Am. Oil Chemists' Soc.*, 37, 486). When methyl oleate was oxidized under oxygen pressure at 120° C., hydroperoxides formed rapidly and the mixture exploded. At 100° C., the rate of peroxide formation was much slower, and no explosion took place (Slover and Dugan, *ibid.*, 635). The rate of oxidation of a mixture of methyl linoleate and dimethylbutadiene was greater than the sum of the rates of reaction of the single materials because in the mixture the two materials were co-oxidized (Kern and Schnecko, *Die Makromolekulare Chemie*, 36, 244). When conjugated fatty acids containing diene through hexaene conjugation, produced by alkali isomerization of codliver oil, tung oil, and ethyl alpha-oleostearate, were subjected to ultraviolet irradiation, all conjugation except diene was destroyed (Kayama and Tsuchiya, *Tohoku J. Agr. Research*, 9, 251).

Four hydroperoxide isomers were formed in the autoxidation of methyl oleate (Privett and Nickell, *Fette, Seifen, und Anstrichmittel*, 61, 842). Pure conjugated *trans-trans* methyl linoleate hydroperoxide was prepared by oxidizing methyl linoleate in petroleum ether solution with oxygen gas, then extracting with aqueous methanol (Banks *et al.*, *Nature*, 184, 816). The course of the oxidation of fatty acids was followed by infrared spectroscopy. Oxides formed more rapidly from *cis* than from *trans* isomers and also formed more rapidly from 9-10 double bonds than from double bonds in other positions. Formation of ketones was detected by ultraviolet spectroscopy (Mironova, *Primenenie Metodov Spektroskopii v Prom. Proizvodstven; Tovarov i Sel'sk. Khoz.*, Leningrad. Gosudarst. Univ. im. A. A. Zhdanova, *Materialy Soveshchaniya, Leningrad*, 1955, 94). The formation of malonaldehyde during oxidation of unsaturated fatty acids was studied quantitatively (Tariadgis and Watts, *J. Am. Oil Chemists' Soc.*, 37, 403). Two geometric isomers of 11,12-dihydroxybehenic acid were isolated from autoxidized cetoleic acid which had been stored for 18 years (Matsuura *et al.*, *Nippon Kagaku Zasshi*, 81, 825). The structures of the dimers that were formed when autoxidized fatty esters and purified fatty hydroperoxides were decomposed at 210° C. in the absence of oxygen were studied (Frankel *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 418).

The effect of solvent on the ozonization of methyl oleate and on the reductive decomposition of the products was studied (Pryde *et al.*, *J. Organic Chem.*, 25, 618).

A review covered the formation, transformation, decomposition, and polymerization of the peroxides of fatty acids and fats (Naudet, *Rev. Franc. Corps Gras, Special Number [J. Etude Alternation Oxidative Corps Gras]* 7, 1959). Because oxygen reacts so rapidly with carbon-free radicals, it was concluded that carbon-carbon bond formation by a free radical mechanism is largely prevented when oils dry in the presence of oxygen (Mayo, *Ind. Eng. Chem.*, 52, 614). The type of aging (polymerization or autoxidation) of an oil was determined from its dielectric constant, refracto-densimetric constant, and iodine value. The former two constants underwent little change during the first stages of peroxidation (Ludde, *Fette, Seifen, und Anstrichmittel*, 61, 1157). The drying of films of dehydrated castor oil (Morgner, *ibid.*, 62, 496), tri-alpha-oleostearin, alpha-oleostearo-dihinolein (Kaufmann and Thomas, *ibid.*, 62, 315), and impatiens oil (Kaufmann and Sud, *ibid.*, 62, 611) was followed by a determination of analytical constants (for the castor oil) or by infrared spectroscopy.

The rate of decomposition of peroxides in various oils was studied. They decomposed more rapidly in oxidized marine and animal oils than in oxidized vegetable oils, and more rapidly in extensively oxidized vegetable oils than in less highly oxidized oils. The accelerating effect of pro-oxidants on the decomposition rate of peroxides in saury oil was not suppressed by the addition of antioxidants (Watanabe and Toyama, *Mem.*

Fac. Eng., Nagoya Univ., 10, 95). Sorbic acid increased the rate of oxygen uptake of butter, lard, and solutions of ethyl linoleate or methyl oleate. In soybean oil, sorbic acid had no effect (Täufel *et al.*, *Nahrung*, 3, 134). Autoxidation under the influence of ultraviolet light was followed by peroxide value and by the benzidine and thiobarbituric acid reactions in the case of olefinic edible fats (Täufel and Zimmerman, *Fette, Seifen, und Anstrichmittel*, 61, 836), by analytical constants and spectroscopic determination of *trans*-isomerism in the case of ethyl oleate, olive oil, and lard (Kuhn and Lück, *ibid.*, 860). The effect of visible light on *beta*-carotene, pheophytin a, and pheophytin b in crude linseed oil was followed by fluorescent and ultraviolet spectroscopy (Kaufmann and Vogelmann, *Farbenchemiker*, 61, 6). The peroxide content of fat from kamaboko and fish meat paste increased markedly on exposure to *gamma*-radiation from cobalt-60 in the presence of air but not in the absence of air (Urakami and Tanaka, *Kaseigaku Zasshi*, 10, 70).

The reaction of aluminum compounds with hydroxylated or oxidized oils or fatty acids produced polymers. Resins were prepared by gelling a hydroxylated glyceride drying oil (*e.g.*, bodied linseed oil) with a small amount of an aluminum compound (*e.g.*, hydroxy isopropoxy aluminum stearate) (Rinse, *U.S. 2,911,316*), also by combining unsaturated fatty acids (*e.g.*, soybean), a hydroxy acid (*e.g.*, ricinoleic acid), and a metal Lewis base (*e.g.*, aluminum tri-isopropoxide) (Chapin and Murphy, *U.S. 2,916,392*). An oxidized drying oil-tall oil mixture or oxidized tall oil alone was cross-linked by reaction with an aluminum compound for use in linoleum (Ayers, *U.S. 2,936,243*; *U.S. 2,936,244*).

Unsaturated fatty acids were polymerized by heating with small amounts of water, a surface-active crystalline clay mineral, and an alkali (Myers *et al.*, *U.S. 2,955,121*). The products of heating linseed ethyl esters at 360° in the absence of oxygen were studied. The presence of iron inhibited the loss of double bonds and promoted the formation of ketones from two molecules of fatty acid (Axt, *Nahrung*, 3, 18). Tall oil was polymerized by heating in the presence of *p*-toluenesulfonic acid (Waida and Terauchi, *Kogyo Kagaku Zasshi*, 62, 1734). A review covered the catalytic isomerization and polymerization of vegetable oils in the presence of sulfur dioxide (Vohwinkel, *Farbe und Lack*, 65, 571). The composition of linseed oil polymerized at 300–330° in the presence of sulfur dioxide and air was investigated by molecular distillation (Boelhouwer *et al.*, *Compt. rend. congr. intern. chim. ind.*, 31^e, Liege, 1958 [pub. as *Ind. chim. belge, Suppl.*] 2, 556). The conditions of manufacture of sulfurized linseed oils with sulfur, SCl₂, S₂Cl₂, or S₂Cl, and the suitability of the products as protective coatings were studied (Schiemann *et al.*, *Fette, Seifen und Anstrichmittel*, 61, 575, 913). Heating fatty acids with boric acid gave products that dried more rapidly than the corresponding triglycerides or pentaerythritol esters. The products were pyrones, formed from four fatty acid molecules. Their use in protective coatings was investigated (Mills and Hammond, *J. Oil and Colour Chemists' Assoc.*, 43, 565). A graphite electrode impregnated with a drying oil was treated with a liquid mixture of chlorine and bromine (Carlin, *U.S. 2,920,004*). The polymerized products obtained from linseed oil by electrical discharge in a hydrogen atmosphere were different from those obtained by thermal or catalytic polymerization (Boelhouwer *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 373).

Drying oils may be improved by processes that increase the number of, or change the location or geometric configuration of, the double bonds in the fatty acid moiety. Codling oil acids were fractionated by means of their addition compounds with urea (Jedlinski and Szpakowski, *Przemysl Chem.*, 37, 648). The solid fatty acids separated from methyl linoleate that had been isomerized with iron pentacarbonyl catalyst were composed mainly of *trans-trans* conjugated dienoic acids, presumably 9,11- and 10,12-octadecadienoic acids (Hashimoto and Shiina, *Yukagaku*, 9, 376). The maximum amount of conjugated dienoic acids in soybean oil isomerized with iron pentacarbonyl was 30%. Isomerization of the oil was more satisfactory than isomerization of the fatty acids (Hashimoto and Shiina, *ibid.*, 79). The intramolecular and intermolecular dehydration of ricinoleic acid (producing linoleic acids and estolides, respectively) at room temperature and higher temperatures was investigated (Hawke and Kohll, *J.S. African Chem. Inst.*, 12, 1). The kinetics of the dehydration of ricinoleic acid at 180° in the presence of anhydrous sodium acid sulfate, producing conjugated 9,11-octadecadienoic acid, were studied (Hawke and Kohll, *ibid.*, 17). The composition of the residue from the distillation of pyrolyzed methyl ricinoleate was studied (Naudet and Vezinet, *Rev. Franc. Corps Gras*, 7, 385). The quality of dehydrated castor oil depended upon the hydroxyl number of the original castor oil, the hydroxyl number of

which could be increased by countercurrent extraction of the oil with petroleum ether (Naudet and Perrot, *Peintures, Pigments, Vernis*, 35, 239). Catalysts for the dehydration of castor oil were studied. An increase in the number of acidic groups in the catalyst increased the rate of dehydration, permitting the dehydration at a lower temperature and reducing the occurrence of side-reactions (Saraf and Dole, *Indian J. Appl. Chem.*, 22, 1). Fractionation of dehydrated castor oil by isopropyl alcohol gave two polymeric fractions with good film-forming properties, a third fraction with poor properties. Dehydration in the presence of 0.2% anthraquinone-1,8-disulfonic acid at 250° gave the highest yield of the desirable fractions (Ambekar and Dole, *ibid.*, 21, 193).

A process for vacuum esterification of fatty acids with glycerol or other alcohols, catalyzed by phosphates of heavy metals, alkali metals, or alkaline earth metals, was described (Milbers, *Ger. 951,070*).

Esters of fatty acids with polyols other than glycerol have a variety of uses. A linoleum cement was prepared by esterifying and oxidizing a mixture of tall oil fatty acids, polyhydric alcohol, and rosin at 160–240° F. in a stream of air (Forsythe, *U.S. 2,937,103*). The polymorphism of fatty di- and tetraesters of pentaerythritol was investigated (Malkin and Gupta, *Fette, Seifen und Anstrichmittel*, 61, 868). A fatty acid-pentaerythritol partial ester was heated in the presence of a sulfonated polystyrene cation exchange resin to produce etherification between free hydroxyl groups (Kraft, *U.S. 2,945,830*). Oleyl, linoleyl, or linolenyl alcohol was heated in the presence of an alkaline catalyst and a boron compound to give a polymeric alcohol of molecular weight 600–800, iodine value 80–95, and hydroxyl content 2.5–3.5%. Esterification of this alcohol with acrylic, sorbic, maleic, or soybean acids gave a drying oil (Gast *et al.*, *U.S. 2,952,556*). Condensation of an acid, such as oleic, with a diaryl-desoxy-glucitol (*e.g.*, 1,1-diphenyl-1-desoxy-glucitol) gave materials useful for preparation of surface coatings, plasticizers, or detergents (Linn, *U.S. 2,909,539*). Fatty mono- through octa-esters of octakis-(2-hydroxypropyl)-sucrose were useful as surface coatings, water-soluble resins, modifiers in alkyl or urethane resins, surfactants, or plasticizers (Melstad, *U.S. 2,908,681*).

Samples taken at various times during the preparation of alkyd resins from linseed, soybean, or tall oil acids showed only minor changes in the iodine values and refractive indices of the acids during processing (Secrest and Kaprielyan, *J. Am. Oil Chemists' Soc.*, 37, 451). Alkyd resins containing tung, oiticica, and *Impatiens* oils along with linseed oil gave quick-drying, hard films, which showed some wrinkling (Kaufmann and Sud, *Fette, Seifen und Anstrichmittel*, 62, 311). Alkyd resins were prepared from the following groups of ingredients: castor oil, dicarboxylic acid, and a polyoxyalkylene compound of 1,700–7,500 molecular weight (Kirkpatrick and Walker, *U.S. 2,925,429*); polyhydric alcohol, polycarboxylic acid, fatty acid, or a partial polyhydric alcohol ester thereof, and a diglycidyl ester of a carboxylic acid (Kammerer, *U.S. 2,951,049*); polyhydric alcohol, vegetable oil or marine oil, and a benzenecarboxylic acid, such as isophthalic acid (Young, *U.S. 2,954,354*). Replacement of 20 to 80% of the fatty acids in alkyd resin with benzoic acid produced resins with improved alkali-resistance (Kraft and Metz, *U.S. 2,915,488*). A process for preparation of alkyd resins involved acidolysis of oils with a phthalic acid, followed by esterification of the acidolysis product with glycerol. Owing to anhydride formation, orthophthalic acid did not react with the oil, but isophthalic and terephthalic acids did react, the former more rapidly than the latter (Carlston, *J. Am. Oil Chemists' Soc.*, 37, 366).

Fatty acids can be converted into polymers or polymerizable materials by other means than esterification with polyols. One such method is esterification with vinyl compounds. Two reviews covered vinyl derivatives of fats, including the preparation and uses of vinyl esters (Uzzan, *Rev. Franc. Corps Gras*, 7, 135; Asahara and Mitsuhashi, *Yukagaku*, 8, 339). Vinyl 12-ketostearate and vinyl 4-ketostearate were prepared, for a polymerization study, by treating the keto acids with vinyl acetate in the presence of mercuric sulfate catalyst (Calderon *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 132).

Fatty derivatives containing free hydroxy and/or carboxyl groups react with isocyanates. Resins based upon fatty materials and isocyanates were prepared from the following groups of reactants: castor oil, glycerol, and tolylene diisocyanate (Toone and Wooster, *Ind. Eng. Chem.*, 51, 1384); polyesters from 9,10-dihydroxy-stearic acid and dibasic acids, and tolylene diisocyanate (Morriss *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 475); a hydroxyaryl aliphatic acid, an active hydrogen compound, and a polyisocyanate (Greenlee, *U.S. 2,907,719*; *U.S. 2,907,745*); a resinous polybasic acid, an active hydrogen compound, and a polyisocyanate (Greenlee, *U.S. 2,907,718*); a

triglyceride with a hydroxyl number above 50, and an organic polyisocyanate. The latter product was mixed with 25-300% of antimony trioxide for use in adhesives, coatings, and films (Szukiewicz, *U.S. 2,943,947*). The reaction of polyisocyanates and polyhydroxy compounds in the presence of water (which reacts with isocyanates to yield carbon dioxide) produces foamed resins. A foamable composition was prepared by reaction of a polyalkylene ether glycol of molecular weight 500-1900 (at least 60% of the glycol was 1,2-propylene ether units), a triglyceride with a hydroxyl number over 100, and an aromatic diisocyanate (Kane, *U.S. 2,955,091*). A composition, consisting of an aromatic polyisocyanate and glycerides of hydroxy fatty acids and diglycolic acid and containing an excess of isocyanate groups, was foamed by the addition of water and a tertiary amine catalyst (Harrison and Brinker, *U.S. 2,921,916*). A castor oil-citric acid ester, containing free acidity, was foamed by the addition of an organic polyisocyanate, water, and a tertiary amine catalyst (Abbotson *et al.*, *U.S. 2,950,263*). A reaction product of pentaerythritol-fatty acid monoester, pentaerythritol dipropional, and tolylene diisocyanate, containing free isocyanate groups, was foamed by the addition of a polyhydric alcohol, water, and a tertiary amine catalyst (Orth, *U.S. 2,936,293*).

Fatty derivatives, containing free hydroxy and/or carboxy groups, also react with epoxy compounds. Drying oil varnishes were prepared by condensation of a diepoxide compound (3,4-epoxy-6-methyl-cyclohexylmethyl 3,4-epoxy-6-methylcyclohexanecarboxylate) with fatty acids to give a material containing residual epoxy groups, and catalytically polymerizing this material (McGarny *et al.*, *Ind. Eng. Chem.*, 52, 318). Other combinations of materials used for the preparation of protective coatings were: castor oil (or blown or acetylated castor oil), glycidyl polyether of 2,2-bis(4-hydroxyphenyl)propane, and an amine epoxy curing agent (May, *U.S. 2,921,040*); a fatty acid and epoxidized Diels-Alder polycyclopentadiene (Greenspan and Light, *U.S. 2,927,934*); drying oil (or semi-drying oil) fatty acids and an epoxidized drying oil (Chatfield, *U.S. 2,909,537*); a monocarboxylic hydrocarbyl acid of 7-20 carbon atoms and an epoxidized hydrocarbon copolymer drying oil, consisting of styrene, methyl, or ethyl ring-alkylated homologues (Millar and Radlove, *U.S. 2,921,947*); drying oil acids (or mixtures of drying oil and rosin acids), styrene, and a resinous epoxide (Edelman, *U.S. 2,909,497*); polyepoxides (including epoxidized alkyd resins or drying oils) and mixed esters of hydroxyaryl aliphatic acids, fatty acids, and polyhydric alcohols (Greenlee, *U.S. 2,907,723*). Products similar to those in the previous reference, by the same inventor, were as follows: mixed esters (*U.S. 2,907,724*); polyepoxide, phenol-aldehyde condensates, mixed ester compositions (*U.S. 2,907,725*); diphenolic pentanoic acid, alkyd acid ester, polyepoxide reaction products (*U.S. 2,907,726*); auto-ester polyepoxide compositions (*U.S. 2,907,727*); compositions of diphenolic acid co-amides and polyepoxides (*U.S. 2,907,728*); epoxide, diphenolic acid aldehyde condensates (*U.S. 2,907,729*); diphenolic acid, epoxide compositions (*U.S. 2,097,730*); epoxide, monohydric alcohol-diphenolic acid ester compositions, and the modification thereof with aldehyde condensates (*U.S. 2,907,731*); polycarboxylic acid, epoxide compositions, and aldehyde condensate modifications thereof (*U.S. 2,907,732*); diphenolic acid-modified oil-aldehyde condensates (*U.S. 2,907,733*); compositions of polyepoxides, ammonia derivative-aldehyde condensates and mixed esters (*U.S. 2,907,734*); esterified epoxy polyesters (*U.S. 2,907,735*); esters of polyhydric phenols (*U.S. 2,907,736*); compositions of novel polyhydric phenols and polyepoxides (*U.S. 2,907,741*); esters of polyhydric phenol amides (*U.S. 2,907,778*); unsaturated diester acids (*U.S. 2,907,779*). Polyglycidyl esters of dimers or trimers of fatty acids were prepared (Newey, *U.S. 2,940,986*).

The introduction of epoxy groups into fatty acids and oils increases their functionality. (See paragraph on plasticizers later in the section for other information on epoxidized fatty derivatives.) Resins were prepared by the curing of mixtures of a diglycidyl ether and an epoxidized oil (lard oil or soybean oil) with phthalic anhydride (Gelb *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 81). A corrosion-inhibiting varnish was prepared from an oleoresinous material (prepared from a drying or semi-drying oil and a resin) and an epoxidized oil or fatty acid (Chatfield, *U.S. 2,930,708*).

Reaction of polyfunctional fatty acid derivatives with polyamines produced polyamide resins. Polyamides were prepared from epoxidized fatty acids (or epoxidized fatty acid-monohydric alcohol esters), hydrocarbon dicarboxylic acids, and polyamines (Delius, *U.S. 2,939,853*). Heat-sealing adhesives were prepared by the reaction of polyamides (prepared from polymeric fatty acids and a polyamine, such as diethylene triamine) with weak polybasic acids, such as succinic, citric, oxalic, or

boric (Aelony, *U.S. 2,908,584*). A polyamide prepared from dimeric or trimeric fatty acids, aliphatic dicarboxylic acids, and a polyamine were added to alkyd resins in small percentages to produce thixotropic coating vehicles (Glaser and Wittcoff, *U.S. 2,932,623*).

Copolymerization is a common means of upgrading fatty acids and oils. The manufacture of copolymers from drying oils and cyclopentadiene and the reaction mechanisms involved were discussed (Kaufmann and Gruber, *Fette, Seifen, und Anstrichmittel*, 61, 743). Adducts were prepared from a low alkyd ester of tall oil fatty acids and an alkyd fumarate (Dazzi, *U.S. 2,938,044*) and from a saturated alkyd ester of an unsaturated fatty acid and maleimide (Tawney, *U.S. 2,948,693*). Other copolymerizations, in the presence of peroxide catalysts, involved the following groups of reactants: fatty acid vinyl esters and acrylonitrile (Asahara and Mitsuhashi, *Yukagaku*, 9, 33); blown soybean or linseed oils and a vinyl chloride-vinyl acetate mixture (Christenson, *U.S. 2,926,153*); drying oils, especially castor oil, and styrene (Menon and Aggarwal, *Paintindia*, 3, 19); a soybean-pentaerythritol-maleic alkyd resin and vinyltoluene (Schwareman, *U.S. 2,912,396*); a heat-bodied oil or a tall oil-pentaerythritol-phthalic alkyd resin, and vinyltoluene or divinylbenzene (Heckles, *U.S. 2,928,796*); an oil-modified alkyd resin, and styrene, an alkylstyrene or divinylbenzene—the catalyst was a tertiary alkyl-substituted diperoxide (Hart, *U.S. 2,919,253*); an oil-modified alkyd resin, an unsaturated acid, such as acrylic, crotonic, or maleic, and styrene, vinyltoluene, or methyl methacrylate (Christenson, *U.S. 2,939,854*). A heat-bodied oil and a vinyl compound, such as styrene, vinyltoluene, or divinylbenzene were emulsion-polymerized in the presence of a peroxide catalyst (Kingston and Schwartz, *U.S. 2,926,151*). A water-dispersible resin was made by preparing an adduct of a drying oil and maleic anhydride, hydrolyzing the anhydride ring, neutralizing with ammonium hydroxide, and then copolymerizing with styrene, vinyltoluene, or α -methylstyrene (McKenna, *U.S. 2,941,968*). The viscosity of a styrenated oil-modified alkyd resin containing a small amount of styrene monomer was increased by heating in the presence of an organic peroxide catalyst (Hart, *U.S. 2,944,991*). The drying properties of oils were improved by heating them at 100-300° in the presence of an alkaline metal addition complex of an acetylenic hydrocarbon or anthracene (Bloch, *U.S. 2,954,387*).

Many 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 simply by the mixing of the various polymeric materials, which causes them to react with one another, or by the mixing and then reaction of the various monomeric materials that would ordinarily go into the preparation of the separate resins. A coating composition consisted of a hydrogenated castor oil-modified phthalic alkyd resin, nitrocellulose, pigment, solvent, and plasticizer (Walus, *U.S. 2,920,054*). Fumaric- and maleic-modified pine oleoresins were used to prepare oil-modified nonphthalic alkyd resins (Halbrook *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 571). A phenol-formaldehyde novolak resin was etherified with styrene oxide, then esterified with drying oil or semi-drying oil fatty acids (Partansky, *U.S. 2,918,440*). A coating for iron or steel was prepared from fatty acids, litharge, sulfur, calcined gypsum, and phenol-formaldehyde varnish (Cophthorne, *U.S. 2,927,089*). Other groups of ingredients used in preparing complex resins were: epoxidized fatty oils and hydrocarbon drying oils, such as polybutadiene or butadiene copolymers (Tulk and Neuhaus, *U.S. 2,907,669*); oil-modified alkyd resin and etherified cyclohexylmelamine-aldehyde resin (Williams and Culbertson, *U.S. 2,916,467*); a dehydrated castor-isophthalic-salicylic-glycerol alkyd resin and butylated melamine-formaldehyde resin, butylated urea-formaldehyde resin, or pyromellitic dianhydride (Mendelsohn, *U.S. 2,945,829*); an alkyd resin or oil-modified alkyd resin with free hydroxyl groups, an aminoplast, and a polyester with free hydroxyl and carboxyl groups, neutralization of the carboxyl groups with ammonia or an ammonium derivative producing a water-dispersible resin (Shelley, *U.S. 2,915,487*); on oil-modified alkyd resin containing free carboxyl groups and prepared from hexachloroendomethylene-tetrahydrophthalic acid and ethoxyline resins. The latter product had improved electrical properties (Rosenberg, *U.S. 2,909,495*).

Alcohol derived from unsaturated fatty acids can be converted into polymeric materials by their first being converted into polymerizable ethers, usually vinyl ethers. The reviews that were mentioned in connection with vinyl esters of fatty acids also referred to vinyl ethers of fatty alcohols. A review described the reaction of soybean and linseed alcohols with acetylene to produce vinyl ethers, the polymerization of the ethers to yield film-forming materials, and the properties of the films

(*Soybean Dig.*, 20 [2], 21). Linseed alcohol and ethyl vinyl ether reacted in the presence of a mercuric acetate-oxalic acid catalyst to give nonconjugated linseed vinyl ether (Brekke and Kirk, *J. Am. Oil Chemists' Soc.*, 37, 568). Conjugated soybean vinyl ether was prepared by treating either conjugated or nonconjugated soybean alcohol with acetylene in the presence of potassium hydroxide (Mustakas *et al.*, *ibid.*, 100). The polymerization of fatty vinyl ethers was more easily controlled when the catalyst was stannic chloride than when it was boron trifluoride. Ferric chloride was an inefficient catalyst (Dufek *et al.*, *ibid.*, 37). Fatty vinyl ethers were copolymerized with other vinyl ethers, and the film properties of the products were investigated, as follows: conjugated soybean vinyl ethers with lower alkyl vinyl ethers (Mustakas *et al.*, *ibid.*, 68); nonconjugated linseed vinyl ethers with lower alkyl vinyl ethers (Gast *et al.*, *ibid.*, 78) and with various other vinyl ethers, most of which contained a phenyl group (DeJarlais and Teeter, *ibid.*, 556). The molecular-weight distributions of some conjugated soybean vinyl ether homopolymers approximated the distribution calculated for simple difunctional polymerization (Teeter *et al.*, *ibid.*, 552). A drying oil alcohol was esterified with methacrylic acid, then combined with vinyl chloride and vinyl acetate (Christenson, *U.S.* 2,946,774). A coating material for baked finishes was obtained by ester interchange between a fatty alcohol and a phenylalkoxy polysiloxane (Olson and Christenson, *U.S.* 2,911,386).

Stearone and methyl heptadecyl ketone were condensed with phenol. The resulting bisphenols reacted with formaldehyde, phosgene, and epichlorohydrin, an indication of potential usefulness as resins (Morriss *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 646).

Reviews covered synthetic resin paints (Yamada, *Yukagaku*, 8, 435) and petroleum chemistry and paints (Toyota, *ibid.*, 323). The following resins, prepared without the use of fatty drying oils, were described: butadiene and styrene, copolymerized in the presence of a hydrocarbon solvent and an alkali metal catalyst, the presence of a small amount of a dihydroxy aromatic compound acting to increase the molecular weight of the drying oil product (Berkeley, *U.S.* 2,925,449); butadiene and styrene copolymerized to a drying oil—the reactants were formed *in situ* prior to the polymerization by the catalytic dehydrogenation of butane and ethylbenzene (Hunt *et al.*, *U.S.* 2,906,787); a linear polyester by reaction, in the presence of a tertiary amine, of allyl glycidyl ether and an acid anhydride (such as phthalic) (Fischer, *Ind. Eng. Chem.*, 52, 321); polyonamide from *omega*-gaminonanoic acid—the latter compound was formed from oleic acid by a series of reactions beginning with ozonolysis (Otsuki and Funahashi, *Advances in Chem.*, Series No. 21, 205); epoxy resins from resorcinol-acetone condensation products (Segal and Rust, *Ind. Eng. Chem.*, 52, 324). Hydrocarbon solutions of polymeric drying oils prepared from oxidized butadiene were stabilized by addition of a liquid saturated alcohol with 1-9 carbon atoms (Koencke, *U.S.* 2,908,585).

The viscosity of a polybutadiene drying oil with an oxygen content of 9% was increased by subjecting the oil to *gamma* radiation in the presence of lead naphthenate (Kirshenbaum *et al.*, *U.S.* 2,936,275). Combinations of poly (alkylene oxides) or other polymer ethers with polymeric poly (carboxylic acids) have water insolubility and other properties different from those of either component alone. This suggested the existence of hydrogen bonding and hinted that this reaction be considered for *in situ* production of hydrophilic elastomers (Smith *et al.*, *Ind. Eng. Chem.*, 51, 1361). The differences between liquid and solid bisphenol A-epichlorohydrin condensates were discussed (Wynstra *et al.*, *ibid.*, 52, 326). A coating composition consisted of cellulose acetate butyrate, solvent, plasticizer, and soybean lecithin (Seaver, *U.S.* 2,927,036).

Miscellaneous formulations involving drying oil products for protective coatings and other uses included the following. A paint for poor paint-holding wood consisted of titanium dioxide, water-ground mica, and a pentaerythritol ester of vegetable oil acids; the vegetable oil had a linolenic acid content below 7% (Schumacher and Mosses, *U.S.* 2,915,411). A vehicle for xitropic paint consisted of an oil-modified alkyd resin, a polyester prepared from a polyhydric alcohol and a polymerized fatty acid, and a calcium drier salt of an organic acid (Cody, *U.S.* 2,922,769). A coating composition contained castor oil, benzol, beeswax, turpentine, and Spar varnish (Hughes, *U.S.* 2,942,995). Addition of a fatty acid salt of a polyamine (such as the oleic acid salt of tetraethylene pentamine) to a paint or varnish reduced the discoloration caused by heavy metal soap driers (Chamot and Ferrara, *U.S.* 2,914,417). A linoleum cement contained an oxidized linseed oil or oxidized tall oil-pentaerythritol ester, rosin, and a metal salt, such as the calcium salt of the dimethylol derivative of p-propylphenol (Graham, *U.S.* 2,918,441). A molding batch for foundry work

consisted of a granular refractory material, sulfur, and a powdered gel of an oxidized drying oil (Lottermoser, *U.S.* 2,927,032).

Polyethylene terephthalate film was coated with a mixture of an oil-modified alkyd resin or a phenol-formaldehyde resin, and amorphous silica or estersils (McBride, *U.S.* 2,921,869). Coating compositions contained a drying oil and a cobalt, manganese, or lead salt of a S_8-C_{20} branched chain carboxylic acid (Kirshenbaum *et al.*, *U.S.* 2,95,949) and an unsaturated fatty acid derivative, also a metal sulfonate (Eastlake and Grummitt, *U.S.* 2,950,982).

Methods for the determination of peroxides, alcohols, carbonyls, epoxides, and total oxidation products in oxidized fats were described (Wolff, *Rev. Franc. Corps Gras*, Special Number [J. *Étude Alternation Oxidative Corps Gras*], 12, 1959). Use of Lindlar catalyst for determination of peroxides was improved (Privett and Nickell, *Fette, Seifen, und Anstrichmittel*, 61, 842). Paper chromatography was applied to the identification of the fatty acids from dehydrated castor oil at each step as they were acetylated, reacted with maleic anhydride, and hydrogenated (Chowdhury, *ibid.*, 924). Other analytical methods included the determination of dicarboxylic acids in modified alkyd resins by titration in ethylene glycol-ethyl alcohol (Esposito and Swann, *Anal. Chem.*, 32, 49); determination of chlorendic acid in alkyd resins by saponification, extraction, and titration (Esposito and Swann, *ibid.*, 680); argentometric determination of epoxides (Krull, *Farbenchemiker*, 61, 23); polarographic determination of metal driers—fatty acids and peroxides interfere (Kuta, *Anal. Chem.*, 32, 1065).

Anhydrous sodium-N-palmitoyl taurate aids in dispersing pigments in waxes, stearic acid, and drying oils (Maxey, *U.S.* 2,919,993). Oil-in-water emulsion pigment colors were prepared by use of fatty acid resin binders, which were emulsion-polymerized or emulsion-aggregated (Auer, *U.S.* 2,907,720) and by use of a pentaerythritol-containing alkyd resin in combination with an amino-aldehyde resin (Auer, *U.S.* 2,907,721). Pigment concentrates consisted of solvent, pigment, soybean lecithin, the condensate of a dialkanolamine ethylene diamine tetraacetic acid and a fatty acid, and a polyethylene glycol-fatty acid ester (Clark and Paul, *U.S.* 2,932,580), and a nonionic alkyl or alkaryl glycol ether miscible in water, a similar glycol ether miscible in hydrocarbon solvents, a hydrocarbon solvent, and a pigment dispersed in a solvent (Bram and Vecchio, *U.S.* 2,942,997).

Fat derivatives are used as plasticizers, principally in polyvinyl resins. A review of this field discussed epoxidized soybean oil, alkyl epoxystearates, epoxidized acetoglycerides, 9,10-trialkyl phosphonostearates, vinyl stearate and its polymers, long-chain alkyl acrylates, vinyl epoxystearate, and condensation products of epoxidized oils with phthalic anhydride (Ault, *J. Oil and Colour Chemists' Assoc.*, 43, 631). A study was made of the relation between structure (chain-length, branching, position of ester linkages) of ester type of plasticizers for polyvinyl chloride (Murai and Akazome, *Kogyo Kagaku Zasshi*, 62, 1094). For plasticizers derived from fats, correlations between structure (double bonds, epoxy groups, ester groups) were studied. Good plasticizers with molecular weights of 300-500 had straight-chain structures and a 2-3 efficient polar groups (Murai and Akazome, *ibid.*, 1098). Unsaturated fatty esters were epoxidized with acetic acid, aqueous hydrogen peroxide, and a sulfonic acid cation exchange resin at 50-100° (Greenspan and Gall, *U.S.* 2,919,283). *Cis*- and *trans*-6,7-octadecenoic acids were epoxidized with permonophthalic and peracetic acids (Faroo and Osman, *Fette, Seifen, und Anstrichmittel*, 61, 636). A laboratory process for continuous counter-current epoxidation, by use of a packed column, was developed and applied to butyl oleate and soybean oil (Latourette *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 559). Epoxidized fatty esters prepared from soybean acids (chiefly linoleic) were superior as vinyl plasticizers to those prepared from camellia acids (chiefly oleic) (Murai *et al.*, *Kogyo Kagaku Zasshi*, 63, 807). The rate of epoxidation of butyl oleate under various conditions was studied (Murai *et al.*, *ibid.*, 803). The decomposition of butyl 9,10-epoxystearate (epoxidized butyl oleate) on heating at 160-220°, alone and in mixture with polyvinyl chloride, was studied (Murai *et al.*, *ibid.*, 62, 1004), as was the rate of acid hydrolysis of this compound under various conditions (Murai *et al.*, *ibid.*, 63, 280).

Epoxidized fatty acid alkyl esters were stabilized against heat degradation by their being heated at 30-100° in the absence of water and in the presence of a solid alkali hydroxide or alkaline earth hydroxide (Gall *et al.*, *U.S.* 2,935,517). The rates of reaction of butyl 9,10-epoxystearate with formic, acetic, and butyric acids were determined (Murai *et al.*, *Kogyo Kagaku Zasshi*, 63, 283). Sperm oil-alkyl fumarate adducts were plasticizers for vinyl polymers (Dazzi, *U.S.* 2,909,536), as were

the products of the reaction of n-butyl fumarate with the dimethylamides of tall oil or tallow fatty acids in the presence of di-tert-butylcatechol (Dazzi, *U.S. 2,913,431*) and the reaction products of alkyl or alkoxyalkyl fumarate (di-n-butyl fumarate), also long-chain nonconjugated dialkyl alkadienedioates (di-n-butyl 1,2-eicosadienedioate) (Dazzi, *U.S. 2,909,500*). Ten maleinated jojoba oil derivatives were tested as plasticizers in vinyl resins and as softeners in Buna-N rubber. Three of the products (those from the methyl ester, butyl ester, and hydrogenated methyl ester of jojoba acids) were comparable to dioctyl phthalate as primary vinyl plasticizers. Two of the products (those from the butyl and hydrogenated butyl ester) met aircraft requirements for low-temperature flexibility in Buna-N (Fore *et al.*, *J. Am. Oil Chemists' Soc.*, 37, 387). Adducts of tung oil with methyl vinyl ketone, dimethyl maleate, methyl acrylate, and acrylonitrile and their hydrogenated counterparts were tested as softeners in Buna-N rubber. Five of the materials met low-temperature flexibility requirements (Placek *et al.*, *ibid.*, 305). Esters for use as plasticizers were prepared from chloromethylnaphthalene and sodium salts of fatty acids (especially oleic and lauric) in the presence of tertiary amine catalysts (Yamashita and Shimamura, *Kogyō Kagaku Zasshi*, 62, 1552). Refined custard apple seed oil could be used as an alkyl plasticizers or in soap manufacture (Naidu, *Indian Oil and Soap J.*, 10, 350).

Miscellaneous products containing fatty materials included a composition intended for use as a paint when mixed with water, containing Portland cement, a stearate water-repellent

compound, and an aliphatic monohydric alcohol with 6-10 carbon atoms (Jones and Jackson, *U.S. 2,953,467*); a tall oil suitable for use in reclaiming rubber, prepared by heating crude tall oil and then adding a stabilizing solution, whereby crystallization of the abietic acid was prevented (Van Valkenburgh, *U.S. 2,908,676*); a hot-melt coating containing oxidized polyethylene wax, a water-insoluble aluminum salt of a saturated fatty acid, and conventional hot-melt coating additives (Rosenbaum, *U.S. 2,943,069*); a protective-coating material for solder, intended to be wiped on the molten solder, consisting of propylene glycol and the diester of ethylene glycol with palmitic acid (Thayer, *U.S. 2,933,412*); a protective coating for the skin, insoluble in water, consisting of a dextran ester of saturated fatty acids with about three fatty acid radicals per anhydroglucose unit (Novak and Tyree, *U.S. 2,954,372*); binary mixtures of polyvinyl acetate and fatty acids, giving monomolecular films stronger than the films from either component alone (*Chem. Eng. News*, 38 [40], 40).

Miscellaneous nonfatty products included pentaerythritol arsenite esters. These could be selectively hydrolyzed, acetyolyzed, or nitrolyzed to produce the corresponding pentaerythritol monoester, the pentaerythritol ester triacetate, or the pentaerythritol ester trinitrate (Stevens, *J. Organic Chem.*, 24, 1715). Synthetic resin, protective coatings were removed from objects by immersion in phenol or cresol containing small amounts of orthophosphoric acid and a wetting agent (Leithauser, *U.S. 2,937,111*). An automatic paint-manufacturing machine was described (Logan *et al.*, *U.S. 2,923,438*).

Report of the Cellulose Yield Committee, 1960-61

THREE SETS of three samples each of linters were sent out to nine laboratories during the past season, 1960-61. All laboratories equipped to run cellulose yield analyses are included in these nine. The following table gives the average results for the three tests.

Lab. No.	No. of tests	A Linter	B Linter	C Linter	Over-all avg. for the year
1	3	78.9	75.0	72.6	75.5
2	3	78.9	75.2	72.5	75.5
3	3	77.7	74.1	71.6	74.5
4	3	78.6	74.8	72.0	75.1
5	3	78.5	74.7	72.1	75.1
6	3	78.5	74.6	71.8	75.0
7	3	78.4	74.5	71.7	74.8
8	3	78.0	73.8	71.0	74.2
9	3	78.2	74.2	71.5	74.6
		78.4	74.5	71.8	74.9

The average analyses of each laboratory are within experimental error. The spread is a little wider than the past year but entirely satisfactory.

No changes are recommended for the method at this time. It is further recommended that samples be sent out at least three times during the next year to check laboratory equipment. The first samples should be sent out no later than the first part of September.

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