Report of the Literature Review Committee*

23rd Annual Review of the Literature on Fats, Oils, and Detergents

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Economic Information and Comprehensive Literature

The domestic production forecast for the fiscal year beginning Oct., 1956, preliminary figures for the year beginning Oct., 1955, and data for the year previous (*Fats & Oils Situation 182*, 29 pp.) on fats and oils are:

	For Year Beginning		
	Oct. 1954	Oct. 1955 (Preliminary)	Oct. 1956 (Forecast)
	Mil. lb.	*Mil. lb.*	*Mil. lb.*
Butter (actual wt.)	1,539	1,580	1,600
Lard and Pork Fat	2,564	2,840	2,625
Edible Beef Fat	269	278	275
Edible Vegetable Oils (plus oil equiv. of seed exported)	5,384	6,113	6,453
Soap Fats (inedible animal fats and marine oils)	3,006	3,313	3,065
Drying oils (linseed, tung, and castor oils)	740	824	687
Others (neats' foot, wool grease, fish liver oil, etc.)	42	31	30
Total	13,544	14,979	14,735

In summarizing the complete data in this publication, it was forecast that large exports and a continued rise in domestic disappearance are likely to reduce carry over stocks of food fats and oils considerably at the end of the present marketing year despite a record output. Total stocks next Sept. 30 as a result may be the lowest for that date since 1951.

Statistics of past years and forecast for 1957 on fats, oils, soaps and detergents, as obtained from the U. S. Bureau of Labor Statistics and Association of American Soap and Glycerine Producers, were published in Chemical Week (Dec. 29, 1956). These data are on production for the various years, prices, and information on employees and their earnings. Economic information on fats, such as availability and uses, in Germany was discussed by Tillmann (*Fette-Seifen-Anstrichmittel 57*, 894).

For an excellent analysis of the soap and synthetic detergent (syndet) industry the reader is referred to the annual review prepared by Dee Snell (*Ind. Eng. Chem. 49*, No. 1, 50A). The production data in this report for 1954 and 1955, and that of 1956 estimated from the first six months figures are as follows:

	1954	1955	1956 Est.
	Mil. lb.	*Mil. lb.*	*Mil. lb.*
Soap	1416	1350	1262
Syndets	2063	2317	2752

Syndets increased 25% in tonnage and 19% in dollar value in the first six months of 1956 with no corresponding decrease in soap sales. He believes that soap is at a level which cannot be reduced until syndet bars begin to encroach seriously on the toilet bar market or until substantial amounts of syndets replace soap in the power laundry.

Economic information sources, production, synthetic and competing materials were the texts of reviews on glycerol (Pasternak—*Soap & Chem. Specialties 32*, No. 2, 45; Pattison—*Ibid.* No. 3, 43). More recently, Dee Snell (*Ind. Eng. Chem. 49*, No. 1, 52A) briefly reviewed the glycerol economics. Production derived from fats was equal to that made synthetically at about 146 million lbs. each. The price has been reduced to 28 cents per lb. which should discourage imports.

Many comprehensive communications were of economic significance because they described sources of fats and fatty oils in a manner to attract or increase commercial interest in them. The text of these were: coconut oil substitutes of India (Tramazi & Bhatti—*Soap & Chem. Specialties 32*, No. 10, 43), quality, production, uses and consumption of coconut oil (*Food & Agr. Org. United Nation Bull. 1956*, 66 pp.), evaluation of *cuscuta europea* for oil production (Simionescu & Grigoras—*Acad. rep. pop. Romane, Studii cercetais stiint 3*, 157), new developments in production of fish oil and meal Rothe—*Fette-Seifen-Anstrichmittel 58*, 431), processing and uses of the seed oil of *Hippophaë rhamnoides* (Kaufmann & Vazquez-Roncero—*Grasas y aceites, Spain 7*, 21), use of *Lallemantia iberica* oil as a drying oil (Petit—*Rev. franc. corps gras 3*, 272), mbocaya palm as a source of oil (Markley—*Econ. Botany 10*, 3; Leow—*J. Am. Oil Chemists' Soc. 33*, 49), classification of olive oils (Martinneghi—*Olii minerali, grassi e saponi, color e vernici 32*, 249), researches on processing olives for oil (Garoglio—*Ibid. 33*, 181), pili pulp oil (Maranon *et al.*—*Philippine J. Sci. 83*, 359), ramie seed oil for making alkyd resins (Popov & Ivanov—*Compt. rend. acad.*

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* LITERATURE REVIEW COMMITTEE

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bulgare sci. 8, No. 2, 17), rice-bran oil (Miyazaki—*J. Utilization Agr. Products 1,* 162), castor oil in industry (Anastasiu—*Rev. chim., Bucharest 6,* 587), utilizing sea lions in Alaska (Dassow—*Com. Fisheries Rev. 18,* No. 1, 5), sunflower oil (Weber—*Urania 19,* 310), tall oil (Young—*Furman Univ. Bull. 3,* No. 4, 135), new methods of processing tallow (Schwitzer—*Fette-Seifen-Anstrichmittel 58,* 167), use of animal fats for feeding cattle (Fevrier—*Rev. franc. corps gras 3,* 24), tobacco-seed oil (Balu & Murthi—*Oils & Oilseed J., India 8,* No. 3, 14; Tugtepe—*Rev. fac. sci. univ. Istanbul 20C,* 280; Schiemann *et al.*—*Fette-Seifen-Anstrichmittel 57,* 1020), seed oil of *Trewia nudiflora* (*Science & Culture, India, 21* 473), turtle oil in cosmetics (Aval—*Rev. franc. corps gras 3,* 105), wool grease and lanolin (Vallee—*Teintex 20,* 681: Garlinskaya—*Masloboino-Zhirovaya Prom. 21,* No. 3, 26), and oils derived from the seeds of *Xanthium strumarium, X. spinosum* and *X. echinatum* (Dima—*Acad. rep. pop. Romane, Studii cercetai stiint. 4,* No. 1-4, 273).

Several reviews pertained to recent research work. Published and unpublished work on fats at the Food Industries Laboratory of C.E.R.I.A. Brussels was comprehensively reviewed (Loncin—*Rev. franc. corps gras 3,* 255). The fat research work at the Hormel Institute was described (Lundberg—*Fette-Seifen-Anstrichmittel 58,* 254). Schwitzer (*Chem. & Processing Eng. 37,* 377) described new developments in oils and fats processing. In a collection of abstracts of papers presented at the convention of the German Fat Chemical Society there were summaries of papers on fat oxidation, nutrition, analysis, processing, detergents and paints (*Fette-Seifen-Anstrichmittel 57,* 871).

Fat Substitutes and Competing Material. Much information on materials which compete with natural fats will appear in the sections on products and detergents. As will be evident, petroleum products and inorganic materials are being substituted for fats in soap and detergent manufacture; organic silicones, silica gels, and resins are being recommended as replacements for metal soaps as grease thickeners; and various resins, plastics, and latexes are being used in place of drying oils in coatings and floor coverings.

Much interest still exists, particularly abroad, in the manufacture of synthetic fatty acids by the oxidation of petroleum (Anastasiu & Wexler—*Rev. chim. Bucharest 6,* 241; Man'kovskaya—*Masloboino-Zhirovaya Prom. 21,* No. 8, 25; Koldovkin & Bodan—*Khim. i Tekhnol. Topliva 1956,* No. 6, 1; Tsyskovskii *et al.*—*Ibid.* 9; Obloj—*Przemysl Chem. 34,* 457; Freidin & Tammik—*Zhur. Priklad. Khim. 29,* 935; Gorin & Rosenstein—*U. S. 2,750,361;* Imhausen & Imhausen—*Ger. 871,008, Cl. 12o*; Pier & Peters—*Ger. 863,195, Cl. 12o*; Walter—*Fr. 992,559;* Szabo & Frazier—*U. S. 2,774,780*). Synthetic fatty materials are also prepared by the hydrogenation of the oxides of carbon (Lemke—*Rev. franc. corps gras 3,* 517; Pfirrmann & Meier—*Ger. 886,448, Cl. 12o;* Wenzel—*Ger. 877,602, Cl. 12o;* Chem. Verwertungsgesellschaft Oberhausen m.b.H.—*Ger. 889,293, Cl. 12o*; Imhausen & Imhausen—*Ger. 886,454, Cl. 12o*).

Biochemical synthesis of fats, although not yet done on a commercial scale, is being investigated. Garcia *et al.* (*Rev. cienc. apl., Madrid 10,* 13) determined the fat synthesizing capacity of 22 species of *Penicillium.* There was a tendency to produce more fat as percent of dry mycelial weight, and per 100 grams of glucose used, when nitrate was the nitrogen sources and when cane molasses was added. *Penicillium lanosum, P. purpurogenum,* and *P. spiculisporum* produced the most lipides of the species tested. Walkers *et al.* (*J. Sci. Food Agr. 7,* 233, 237) similar work indicated that ammonium nitrate was the best nitrogen source; best fat production was obtained with xylose, glucose, maltose and inulin as the carbohydrate source; and addition of corn steep liquor and definite concentrations of certain inorganic salts were conducive to fat production. Cultures of *Aspergillus nidulans, Penicillium spinulosum,* and *P. javanicum* were used in these investigations. With a mixed culture of yeasts grown in a sulfite waste liquor medium under aerated conditions, the presence of phosphates increases growth of cells with low fat content; whereas, at low phosphate content the division time of cells is longer but the cells have a high fat content (Schulze—*Appl. Microbiol. 4,* 207). Yeasts grown in a medium in which the concentration of the growth factor, inositol, was reduced below normal levels resulted in cells which were easily ruptured to yield a high proportion of fatty substance (Challinor & Daniels—*Nature 176,* 1267). A method of producing glycerol by yeast fermentation was patented (Frankel & Goldheim—*U. S. 2,772,206-7*).

Photosynthesis and formation of fats in a diatom, *Naviculla pelliculosa,* was studied (Fogg—*Ann. Botony, London 20,* 265). The data presented pertains to the effect of light intensity, nitrogen source, and amount of nitrogen compounds present on the amount and character of the lipides produced.

New Comprehensive Literature. The previous review of this series was published in *J. Am. Oil Chemists' Soc. 33,* 203, 240. A review of like scope was prepared by the members of the Fat and Oil Group of the Society of Chemical Industry (*Prog. Applied Chem. 40,* 207). A published lecture given by Shorland (*Australian J. Sci. 18,* No. 4A, 49) was on new trends in fat research. A new Russian journal entitled "Problems of Selection and Agrotechnics of Soybeans" began publication.

The new books of interest to fat, oil and soap chemists that came to the reviewer's attention during the year were:

Am. Soybean Assoc.: The Soybean Blue Book 1955. 160 pp. $3.00.

Becker, C., Jr. & Lödl, A.: Neuzeitliche Wachswaren und ihre Herstellung. Tl. I. Reinigungs- und Pflegemittel für Leder, Möbel, Fussböden und Autos. Tl. II. Kerzen und Wachswarten. Augsburg: H. Ziolkowsky 1954, 332 pp. DM 23.70.

Brit. Launderers Assoc.: Laundry Chemistry, 1955. 152 pp.

Coatti, G.: Lindustria dei detersivi. Milan: U. Hoepli, 1956. 306 pp. L. 1500.

Daubert, B. F. (Ed.): Fats-Oils-Detergent Yearbook 1955. New York: Interscience Pubs. 1956. 1150 pp. $45.00.

Brown, W.: The Principles of Laundering. London: Heywood & Co. 1955. 104 pp. 15s.

Gavrilenko, I. V.: Poluchenie Khlopkovogo masla na ekstraktorakh nepreryvnogo deistviya (Cottonseed Oil by Continuous Extractors). Moscow: Pishchepromizdat 1955. 90 pp.

Hadert, H.: Technische Fette und Wachsgemische. Berlin: Hadert-Lexicon-Verlag. 1956. 231 pp. DM. 14.80.

Hilditch, T. P.: The Chemical Constitution of Natural Fats. 3rd Ed. 1956. New York: John Wiley & Sons. 1956. 664 pp.

Holman *et al.* (Editors): Progress in the Chemistry of Fats and Other Lipids. Vol. III. London: Pergamon Press. 1955. 475 pp. 70s.

Leghissa, S.: Manuale pratico per la fabbricazione delle cere, creme, lucidi. Florence: Cya. 1954. 132 pp. L. 800.

Lüttgen, C.: Glycerin und glycerinähnliche Stoffe. 2nd ed. Heidelberg: Strassenbau, Chemie u. Technik Verlagsges 1955. 198 pp. DM 28.

Nevolin, F. V.: Khimiya i tekhnologiya proizvodsta glitserina (Chem. and Tech. of Glycerol Production). Moscow; Pishchepromizdat. 1954.

Strausz, H. J.: Manufacture of Glycerol. 2nd ed. London: Tech. Press. 1956. 300 pp. 70s.

Truter, E. V.: Wool Wax. Chemistry and Technology. New York: Interscience Pubs. 1956. 378 pp. $8.75.

A list of reference books useful as sources of information on properties, chemistry, biochemistry, and technology of fats, oils and their derivatives has been compiled (Piskur—*J. Am. Oil Chemists' Soc. 33,* No. 5, Suppl. 22).

Two series of lectures, equivalent to comprehensive books, have been published. These were on, respectively, Unit Processes in the Fatty Oil, Soap and Detergent Industries (*J. Am. Oil Chemists' Soc. 33,* 453), and Oil Mill Operating (*Oil Mill Gaz. 61,* No. 6, 15; No. 7, 21). Another series of papers which is continuing from the past few years, is on production, transport, storage and processing in the fat and oil industry (Kaufmann & Thieme—*Fette-Seifen-Anstrichmittel 57,* 1040; *58,* 49, 131, 196, 274, 363, 458, 661, 539, 661, 782, 921).

Production Processes

Animal and Fish Fat Production. Newly designed rendering methods reflect the search for techniques which permit continuous operation. In one process fatty tissue was comminuted to form a slurry, heated to the melting point of the fat and separated into fat and a source for gelatine (Sifferd & Anderson—*U. S. 2,748,152*). In other similar processes, with which there was no interest in gelatine production, the slurry was heated to precipitate the protein which could then be separated by either filtration or centrifuging (Dufault—*U. S. 2,742,488*), Lapshin—*Myasnaya Ind. S.S.S.R. 27,* No. 5, 22). In a technique using coarse grinding, the protein was separated by filtration (Dayen & Christensen—*U. S. 2,745,856*). A solvent process for animal tissue comprised, comminuting, shaping into thin sheets, searing to inhibit adhesion and passing through perchlorethylene vapor and hot liquid to dry and degrease (Low—*U. S. 2,742,489*).

Ultrashort wave of 50 Mc. was used in rendering to heat tissue or bone (Saito—*Bull. Natl. Inst. Agr. Sci., Japan, Ser. G,* No. 4, 69). The process produced lard and bone oil of much greater stability than those produced by boiling or autoclaving.

Data from operation of an impulse bone degreaser in Russia were recorded (Petrovskii—*Myasnaya Ind. S.S.S.R. 27,* No. 1, 9). Such processes are based on liberating fat by subjecting ground bone to repeated intense impacts delivered through a liquid media. The method has also been patented for the deoiling of seeds (Chayne—*U. S. 2,773,082*).

Okura *et al.* (*Repts. Research Lab. Nippon Suisan Co. 7,* 39, 43, 46, 51, 57, 67, 70, 72, 84, 89, 92, 95), determined the processing conditions for the Kvaerner and the Hartmen renders, used on whale factory ships, that give optimum yield and quality of product at least cost. Mukai (*Bull. Japan Soc. Sci. Fisheries 21,* 187, 190, 921), who earlier suggested that the pigments of highly colored whale oils were iron and pyrrole compounds and were derived from blood, has now confirmed this with tests on raw whale blubber and horse hemoglobin. The discoloration increased with the amount of hemin and did not occur in aqueous solutions without the presence of whale oil. Experimental rendering of dolphin oil has shown that at 65–73° in carbon dioxide atmosphere or reduced pressure 69–70% fat was obtained from subcutaneous tissue in one hour (Rankov & Ivochev—*Compt. rend. acad. bulgare sci. 7,* No. 3, 49; *8,* No. 1, 41). Increasing the temperature or time did not increase the yield or vitamin A content of the oil. Rendered *Theragra chalcogramma* liver oil contained less unsaponifiable matter than that obtained by ether extraction (Toyama & Takai—*Research Rept. Nagoya Ind. Sci. Research Inst. No. 8,* 46).

A Wisconsin plant for continuous butter or butter oil making directly from fresh whole milk was described by Davis & Roahen (*Food Eng. 28,* No. 4, 50). Pasteurized summer cream with 45–60% fat, frozen at —10° or —25° and kept at these temperatures for 6–7 months when thawed and converted to butter gave a product equal to winter butter and superior to stored summer butter. (Meyknecht—*Neth. Milk Dairy J. 10,* 18). The practice of farmers of adding new cream to stored cream before marketing masks the apparent decomposition of the stored cream, but this decomposition was evident in the finished butter through a test for water insoluble acids (Hillig & Jordan—*J. Assoc. Off. Agr. Chemists' 39,* 454). A test under commercial conditions in 29 Canadian creameries has shown that there were no significant differences in the flavor quality of comparable washed and nonwashed butters before and after storage (White *et al.*—*J. Dairy Sci. 39,* 261, 1351, 1359). Data on the course of the peroxide value, acidity, flavor, copper and iron content, and bacterial count were recorded in this work. Test on chlorination of butter wash water has shown that 5 p.p.m. of available chlorine was usually adequate, and that grade score or storability of the butter was not affected until about 75 p.p.m. was reached (McDowall & McDowall—*Australian J. Dairy Tech. 11,* 52). The flavor of foods like butter which contain diacetyl was said to be improved in stability by addition of butyl alcohol (Merker—*U. S. 2,773,772*).

A process for making butter without churning comprised mixing cream having a high fat content with butter at 17–33° until substantially uniform (Goede—*U. S. 2,729,563*).

Various structures in butters were microscopically observed on microtome slices and were discussed in regard to production methods (Gavél—*Z. Lebensm.-Untersuch. u. -Forsch. 104,* 1; *Fette-Seifen-Anstrichmittel 58,* 603). The poorly kneaded or brittle hard butter contained water pathways and was fissured in structure.

General papers on butter were on the theories of butter formation (Mohr & Mohr—*Milchwissenschaft 10,* 117), a review on churning, kneading, consistency, color, antioxidants, etc. in butter making (Mohr—*Fette-Seifen-Anstrichmittel 57,* 925), and contributions of industrial research to butter manufacture (Thomsen—*J. Dairy Sci. 39,* 819).

VEGETABLE OIL EXTRACTION. General descriptive and review communications on vegetable oil processing were written on: cottonseed oil milling by solvent extraction (Bagot—*Oleagineux 10,* 723, 815), control of flow and temperatures in soybean oil extraction (Spencer & Weyermuller—*Chem. Processing 19,* No. 6, 10), modern methods of olive oil production (Garaglio—*Rev. franc. corps gras 3,* 646), interfacial tension between oil and water in olive pastes in regard to extraction (Martinez-Moreno *et al.*—*Grasas y aceites, Spain 7,* 5), the Russian "EP" expeller press (Chernov—*Myasnaya Ind. S.S.S.R. 27,* No. 1, 19), protein deterioration in oil-extraction processes (Leont'evskii & Fal'k—*Masloboino-Zhirovaya Prom. 21,* No. 3, 13), and processing cottonseed by partial deoiling in a press followed by solvent extraction (Gavrilenko & Bezuglov—*Ibid.* No. 8, 5).

The treatment of cotton plants with maleic hydrazide to inhibit secondary growth seemed to inhibit free fatty acid formation in the seed during field exposure and during storage at relatively high humidity; and to inhibit the slow rate of free fatty acid formation by the seed itself in absence of mold growth (Lambou *et al.*—*J. Am. Oil Chemists' Soc. 33,* 199). Oil losses in cottonseed hulls were reduced to a minimum when the seeds were at 8.5–9% moisture content during hulling (Markman—*Masloboino-Zhirovaya Prom. 21,* No. 2, 7). Respiration and heating of sunflower seeds in bins was prevented by reducing the moisture content to 7.0–7.5% (Kopeikovskii *et al.*—*Ibid.* No. 3, 5).

Some unconventional methods of oil extraction were patented. Fresh coconut meats were shredded, pressed, the juice centrifuged to produce a "cream" of 85% oil content, and oil was recovered from the cream by chilling and rapidly heating to 25–40° to break the emulsion (Robledano—*U. S. 2,742,487*). Seed material was ground to a slurry in alkaline aqueous solution at pH of optimum protein solubility, the pH was lowered to precipitate the proteins, the emulsion was separated and adjusted in pH and temperature to release the oil (Sugarman—*U. S. 2,762,820*). Good quality proteins are derived through this process. Vegetable oils were also extracted with soap solutions at temperatures just below the coagulation temperature of the protein to yield insoluble fibers and an emulsion which was separated into oil and protein plus carbohydrates (Kao—*U. S. 2,773,889*).

Solvent extraction equipment has been designed to first dry vegetable and animal products in hot solvent vapors, separate moisture from solvent, and use the solvent to extract the dried product (Cinquinä—*Ital. 488,006; 494,106*). Equipment was designed for solvent extracting oils under pressure and at high temperatures (Lipovatz—*Ital. 489,577*). Because high temperatures activate the diffusion process and reduce viscosity of the miscella such processes should have some economical advantages (Antonioli & Turriziani—*Ann. chim., Rome, 45,* 1035). New equipment was designed to leach, drain, and successively wash a series of charges with solvent (Andrews—*U. S. 2,726,939*). Use of positive pressure to exhaust chambers containing such charges was also patented (Andrews—*U. S. 2,733,136*). Another new system was based on successively grinding the oily material in hot chlorinated solvent (McDonald—*U. S. 2,752,377*). Using this system, the fatty material in both animal and vegetable products can be stored as a slurry in large tanks until completion of extraction, thus retarding deterioration of the fatty materials (Pominski & Vix—*U. S. 2,729,661*).

Experimental data were recorded and suggestions were made for preparation of flaxseed (Knoepfler *et al.*—*J. Am. Oil Chemists' Soc. 33,* 372), sesame seed (Graci *et al.*—*Ibid.* 645) and cottonseed meats for extraction (Spadaro *et al.*—*Ibid.* 177). Instructions for the first two seeds mentioned pertain to method of milling, cooking with moisture adjustment, and crisping. With cottonseed the cooking was done in solvent and better "Filtration-Extraction" characteristics were attained when a combination of lye and salt was added.

Several communications pertained to processing conditions for cottonseed to produce good quality products. Successively, stepwise extracting raw and cooked seed meats demonstrated that cooking reduced the amount of impurities in the solvent extracted oils, and that the more exhaustive extractions contained the greater amounts of undesirable non-neutral oil material (Eaves—*J. Am. Oil Chemists' Soc. 33,* 639). Cottonseed flakes, mixed with a dilute solution of borax and dried, yielded light colored oil either by solvent extraction or pressing (Maki—*Japan 6437-'54*). A comparison of cooking cottonseeds at various pH levels has shown that a high pH was conducive to production of oils with low refining loss, low gossypol content, and not subject to reversion (King *et al.*—*J. Am. Oil Chemists' Soc. 33,* 71). The meals produced in this work show high nutritive value from treatments at pH's 4.5–5.5, a dip in nutritive value near the neutral point, and another high level around 6.5–8.5. These observations were the basis for a patent on obtaining meals of improved nutritive value (King *et al.*—*U. S. 2,726,155*).

Investigations on toxicity and other properties of gossypol are pertinent to processing of cottonseeds for this constituent must be removed from the products or inactivated. On heating a solution of gossypol in refined sunflower oil the gossypol decreased slowly at 80°, abruptly to a constant value at higher temperatures; and this disappearance was quite marked in the presence of peroxides (Markman & Kolesov—*Zhur. Priklad. Khim. 29,* 424). It was suggested that peroxides and dissolved oxygen contribute to the destruction of gossypol. New biological tests have confirmed and amplified conclusions reported earlier that free gossypol content of cottonseed meal is not a true measure of its toxicity (Eagle *et al.—J. Am. Oil Chemists' Soc. 33,* 15). In the same studies it was also demonstrated that there was poor correlation between biologically evaluated protein quality of cottonseed meals and their protein solubility in 0.02 *N* sodium hydroxide. Other work has shown that if cottonseed meals were fed to chicks as 40% of the total ration the free gossypol content of the meal would have to be greater than 0.15% (commercial meals do not contain this much) before gossypol toxicity would appear (Couch *et al.—Poultry Sci. 34,* 178). The conclusions from another study suggested that the free gossypol content of diets should not be greater than 0.016% when they are fed to white leghorn chicks or greater than 0.020% when fed to New Hampshire chicks (Heywang & Bird—*Ibid.* 1239).

Optimum conditions recommended for obtaining high-quality soybean press-cake and oil were to increase moisture content, age for at least four hours, and cook and press at 95° and 105° respectively (Rzhekhin *et al.—Masloboino-Zhirovaya Prom. 21,* No. 6, 9). Smith *et al.* (*J. Am. Oil Chemists' Soc. 33,* 360) have graphically recorded the decrease of urease activity of soybeans with autoclaving and standardized the test for this activity. The graphs are useful for the design of soybean cooking operation. Viscosity and density data of soybean- and sunflower-benzine miscella recorded by Belobordov (*Masloboino-Zhirovaya Prom. 21,* No. 3, 11) are useful for the design of solvent extraction processes. A patented process for recovery of hexane from soybean cake was based on sweeping it with carbon dioxide while in a dryer, recovering the hexane from the gases and recirculating the carbon dioxide (Tamaoki—*Japan 7237-'54*).

Good quality neutral oil was extracted from olive pomace by drying to five percent moisture, mixing with soda ash, and extracting with carbon disulfide (Proto—*Ital. 486,850*).

In a comparison of three petroleum solvents for extraction of corn oil, hexane and isoheptane were better extractants than heptane at the same temperature; and hexane at 157°F. was equal to isoheptane at 192°F. (Arnold & Rowe—*J. Am. Oil Chemists' Soc. 33,* 396). Specimens of trichloroethylene-extracted meals which were of known high toxicity to cattle were nontoxic, even at very high levels, to swine (Hanson *et al.—J. Animal Sci. 15,* 368) and to various domestic poultry (Hill *et al.—Poultry Sci. 35,* 686; Balloun *et al.—Ibid.* 163).

Loury (*Rev. franc. corps gras 3,* 93) compared acetone (10% water) with hexane, cyclohexane, methyl ethyl ketone, methanol, trichloroethylene, and dichloroethylene for the extraction of peanut oil. The acetone seemed desirable on the basis of safety, heat of vaporization, efficiency, and quality of oil. Curves on extraction efficiency in relation to moisture content were recorded. In similar investigations on rice bran oil production, ethanol was considered more desirable than gasoline, benzene or chlorinated hydrocarbons (Rao & Murthy—*Bull. Central Food Tech. Research Inst., Mysore 4,* 205). The record of this work contained information on preparation of the bran for extraction, optimum extraction conditions, characteristics of products, and character of the oil after refining and bleaching. Fundamental data for use of aqueous ethanol as a solvent for extraction of corn, linseed, tung, babassu, coconut, olive, palm, rapeseed, and sunflower-seed oils were developed by Rao & Arnold (*J. Am. Oil Chemists' Soc. 33,* 82, 389). The principal data in this work are the curves of critical solution temperature *versus* aqueous-alcohol composition for the oils. Extraction of tung kernels or meals with alcohol produces meals that are nontoxic to either chicks or rats, but the quality of the protein is too low to offer much promise as an economical source for protein. (Lee—*J. Agr. & Food Chem. 4,* 67). Lipides which cannot be extracted by alcohol alone, such as some sterols and phosphatides, yield to alcohol extraction along with the easily extractables, when the lipide containing material is treated with normal short organic acids or their anhydrides, amides or other derivatives of the acids (Owades & Breivik—*U. S. 2,753,362*).

Byproduct Fats. Tall oil was removed from unsaponifiable materials by dissolving in methyl isobutyl ketone and precipitating the oil with urea (Drechsel—*U. S. 2,717,890*). Good quality fatty acids were produced from tall oil by refining, bleaching, and fractionally distilling (Yoshii—*Japan 6730-'54*). Fatty acids were produced from guayule resin by saponifying, extracting with organic solvent to remove unsaponifiable, and acidifying the residue to recover the acids (Weeks & Banigan—*U. S. 2,744,125*).

Studies on equilibrium distribution of wool fat between fiber and solvents and effect of solvent circulation rate on extraction has indicated that the rate of extraction is principally controlled by diffusion through the liquid film of solvent (Bhat—*Trans. Indian Inst. Chem. Engrs. 6,* 51). Liquids from degreasing of wool were adjusted to a pH range of 8–12 with alkali and centrifuged to recover a neutral wool fat (Chabrand—*Industrie textile No. 822,* 337). A patented method of wool recovery was based on froth flotation in equipment comprising aerated flotation cells, stirrers, impellers and collectors (Evans *et al.—U. S. 2,765,081*).

A solvent extraction process for production of oil from fermentation residues involved the use of the solvent in the vapor phase for better penetration (Metalurgica Naval y Terrestre S. A.—*Span. 225,195*).

Refining, Bleaching, and Deodorization. Certain oils are degummed as a complete refining while degumming in other oils is for the purposes of reducing losses and other advantages in other conventional refining procedures. Degumming of soybean oil by hydration at 120–180°F. to decrease the phosphatide content to 0.023–0.3% followed by deodorization was said to produce a nonreverting light-colored edible oil suitable for use in salad dressings, margarine and other foods (Werly—*U. S. 2,746,867*). Treating solvent extracted oils with ketone before the degumming by hydration was said to yield stable oils which can be decolorized by heating (Wolff & Hayes—*U. S. 2,754,309*). Treating a soybean oil with 0.1% acetic anhydride at 60° followed by degumming by hydration was said to produce a product of quality comparable to alkali refined oil (Hayes & Wolff—*J. Am. Oil Chemists' Soc. 33,* 440). A preliminary treatment of oils with ammonia to remove gums and part of the free fatty acids reduced overall refining losses and produced high quality gums of low glyceride content (Clayton—*U. S. 2,769,827*).

The presence of a small amount of aqueous solution of sodium hydrosulfite in a crude oil permitted adequate refining without using an excess of alkali, thus gaining the advantage of low oil loss (Sadler—*U. S. 7,732,388*). In a refining system aimed at obtaining a high yield of sterols from the foots, the oil was emulsified with alkali, emulsion breaking agents were added, and the mixture was submitted to shear followed by centrifuging (*Julian—U. S. 2,752,378*).

New development for continuous alkali refining were described. One new continuous process was based on circulating a gas-permeated mixture of oil and alkali through vertical pipes (Milbers & Sondermann—*U. S. 2,733,253*). An improvement in a two-stage continuous refining system pertained to blowing steam through the mixture during the first alkali treatment (Afzelius—*U. S 2,729,662*). Conditions recommended for continuous refining of rapeseed oil were hydration with steam, holding 2 hrs., centrifuging, and alkali refining with 100% excess alkali, based on free fatty acids (Zharskii and Romanova—*Masloboino-Zhirovaya Prom. 21,* No. 8, 12). A potentiometric method has been designed for checking alkali delivery of proportioners in the continuous soda ash process of refining of oils (Mattikow & Edmonds—*J. Am. Oil Chemists' Soc. 33,* 439). A centrifuge was designed for continuous oil refining systems which separates refining mixes into three fractions: refined oil, spent lye, and soap (Zacharissen—*U. S. 2,752,089*). A control test method for determining the completeness of washing alkali from refined oils was based on the color developed on addition of phenolphthalein indicator to a standard water extract of the oil (Styazhkina—*Masloboino-Zhirovaya Prom. 22,* No. 4, 18).

A new soda ash refining process involved treating the oil with 22° Bé soda ash solution at a concentration 2.5–3 times that required to neutralize the free acids in a zone at 180–200°F., degassing, and then centrifuging (Smith & Aryes—*J. Am. Oil Chemists' Soc. 33,* 93). In this process fatty acids may be recovered from the foots by liberation with sulfuric acid and the sodium sulfate formed can be used in rehydration of the oil (Thurman—*U. S. 2,759,957*).

In an investigation on refining variables, it was observed that high shear as compared to standard mixing in most cases reduces color, and was more effective in removing gossypol-like and carotenoid pigments; and this effect of high shear was most evident as the temperature during refining decreased (Feuge *et al.—J. Am. Oil Chemists' Soc. 33,* 344). In batch refining, the presence of a brine underlayer during the neutralization resulted in 1–2% higher yield than those of the conventional batch refining process (Zuromski—*Przemsl Spozywczy 10,* 203). Investigations on changes of characteristics of oils during refining show that there is usually a decrease of iodine value in the refined oil, whereas the soap stock has a higher iodine than the original oil (Janick *et al.—Prumysl Potravin 7,* 213). In this work, linseed oil was an exception for the reverse was observed.

Special refining procedures were designed for certain oils. Crude cottonseed oil of high acid number was dissolved in an equal volume of benzene before alkali refining (Kimoto—*Japan 1077-*'55). Methods designed for chrysalis oil (Ikeda—*Japan 7238-*'54) and karanja oil (de Sa *et al.—J. Sci. Ind. Research, India, 14B,* 358) were based on neutralizing in three stages at increasing temperatures and with higher concentrations of lye, respectively. Yellowish-brown fish oils were refined by treatment with dichromate and acid followed by neutralization with lye (Fukushima & Tanaka—*Japan 335-*'55).

Low molecular weight alcohols were used to remove free fatty acids from crude oils. In a continuous refining process, oil in the form of miscella was extraction solvents is treated with an acid and then washed with aqueous alcohol solutions (Weber—*U. S. 2,739,164*). In tests on deacidification of corn oil, the alcohol selectively extracted free oleic acid (Venkataraman & Laddha—*J. Madras Univ. 25B,* 219). In one system for refining karanja oil, it was washed four times with 90–95% ethanol, subjected to mild steam distillation, and refining was completed with lye (Council Sci. & Ind. Res.—*Indian 47,* 802).

Highly acid rice bran oil was refined by dissolving in commercial hexane, chilling to precipitate wax, boiling with mineral acids, bleaching with earth, and reesterifying the free fatty acids with glycerol (Martinenghi—*Olearia 9,* 201).

Cottonseed oil foots was made suitable for animal feeding through heating at 210–220° to reduce the gossypol content to less than 0.02% (Pack & Goldblatt—*U. S. 2,746,864*).

In experiments designed to prevent color reversion in stored, cured cottonseed oils by treatment with various amines, only *p*-aminobenzoic acid formed an oil-insoluble derivative with the color precursor of the oil, gossypol (Dechary & Brown—*J. Am. Oil Chemists' Soc. 33,* 76).

An integrated refining process of a salad cottonseed oil plant contained such features as soda ash treatment of meats before extraction, alkali refining under exclusion of air and winterizing while the oil is still dissolved in the miscella, and adding the foots to the meal produced (Cavanagh—*J. Am. Oil Chemists' Soc. 33,* 528).

Two items were of general interest to refiners. Operating technique was described for using woven wire cloth filters in place of textile cloths and papers in plate filter presses used for filtering foots from crude oils (Grim—*Ibid.* 437). It was suggested that compressed air provides a handy means of transporting liquids and it eliminates pumps (Walter—*Chem. & Processing Eng. 37,* 392).

Several general information and review communications were written on bleaching of fatty oils. The subjects of these were: bleaching of fats and oils (Wittka—*Seifen-Öle-Fette-Wachse 81,* 752), chemical bleaching of fat products (Kreuger—*Ibid.* 528), bleaching cottonseed oil with anionic-exchange resin (Ninni & Ninni—*Prakt. Akad. Athenon 28,* 285); treatment of linseed oil with activated fuller's earth (King & Hutchinson—*J. Oil & Colour Chemists' Assoc. 38,* 673); using Neyveli clays for bleaching oils (Rao & Reddy—*J. Ind. Chem. Soc., News Ed., 18,* 65), and Indian bentonite in refining of vegetable oils (Chaliha *et al.—Sci. & Culture, India, 21,* 161); the bleaching effect of oxidation, hydrogenation, high temperatures, adsorbents, and deacidification on the natural pigments contained in vegetable fats and oils (Bertram—*Rev. fermentations et inds. aliment. 10,* 203); and surface area of some commercial adsorbent bleaching earths (Paleni—*Olii minerali, grassi e saponi, colori e vernici 33,* 229).

A continuous bleaching system was based on proportioning bleaching earths into the systems in the form of oil pastes (Hugel & Spangenberg—*U. S. 2,768,747*). A combined detoxifying and bleaching method for cottonseed, linseed and other oils comprised dissolving the oil in organic solvent and passing it through columns containing active carbon or alumina and then through alkaline adsorbent (Siebel-Rupp—*Fr. 991,878*). Rapeseed oil was decolorized by washing with dilute alkali and heating at 250° for five minutes (Kajizuka & Akatani— *J. Yamagata Agr. Forestry Soc. No. 7,* 18; *No. 8,* 9, 98). The use of alkaline salts such as soda and trisodium phosphate in a similar system was patented (Afzelius—*U. S. 2,754,310*).

In bleaching with sodium chlorite, the formation of stable chlorinated fatty acids was prevented by buffering to a pH of 4.5 with acid salts (Jacini—*Olii minerali, grassi et saponi, colori e vernici 33,* 2; *Fette-Seifen-Anstrichmittel 57,* 903). Bleaching fatty oils with 98–99% sulfuric acid with subsequent washing and neutralization was patented (Vazquez—*Span. 223,108*).

The basic features of a new continuous fat deodorizer are means of flowing thin films of oil under vacuum into shallow pools and emitting steam through the pools to splash oil against porous baffles to increase contact of oil with steam (Thurman—*U. S. 2,759,883*). Other patents on deodorizers pertain to the structural features of the splash plates and the hood above them (Miller & McMichael—*U. S. 2,743,915–916*). Apparatus, details of operation, and useful notes were presented for deodorizing oils in plants handling about 40 tons per day (Berti—*Rev. franc. corps gras 2,* 863). A chemical method of deodorization involved treating the oil with concentrated aqueous solutions of sodium bisulfite and potassium bromide (Okume & Okume—*Japan 7588-*'54).

Passing rancid edible fats through a column of silica gel was said to regenerate them for edible purposes (Loury—*Fr. 990,704*).

BYPRODUCTS OF REFINING. Sugar cane oil contains about 10% wax which can be recovered by precipitation with acetone and used for the production of fatty alcohols (Hill—*U. S. 2,719,858*). A liquid wax was produced from crude sperm whale oil by counter-current fractionation with a liquefied normally gaseous hydrocarbon (Brabets *et al.—U. S. 2,730,538*). The alcohols derived from this wax were fractionated into saturated and unsaturated components through utilizing a differential solubility of these in liquid ammonia (Itai—*Repts. Res. Lab. Nippon Suisan Co. 7,* 97, 102, 108; Sakai—*Japan 1369-*'55). Solvent fractionation with ammonia in this work also permitted the separation of a kitol-vitamin A concentrate from whale liver oils.

An examination of recently patented and commercial methods for production of vitamin A concentrates from fish liver oils has indicated that methylation followed by molecular distillation is economical and yields a potent concentrate (Higashi *et al.—Bull. Japan Soc. Sci. Fisheries 20,* 328, 337). Fractionation or destearinization permits some concentrating of vitamin A because the vitamin concentrates with the more unsaturated oil fractions (Passino—U. S. 2,730,484; Inagaki & Matsuda—*Bull. Japan Soc. Sci. Fisheries 21,* 42). Other methods described for concentration of vitamin A were based on industrial molecular distillation (Tsujino & Kikuchi—*J. Agr. Chem. Soc. Japan 27,* 437) and on a commercial process of separating the unsaponifiable matter and recrystallizing this from methanol (Ishizaka & Hori—*Japan 1384-*'55). A means of converting vitamin A concentrate derived from fish oils to a deodorized product comprised dissolving in cottonseed oil and distilling with a molecular still (Suzuki—*Japan 6438-*'54). The first fraction is dark and odorous, hence is discarded. The concentration of carotene and/or tocopherols from palm oil by a thermal diffusion process (Jones & Milberger—*U. S. 2,741,643*), and by converting the oil to methyl esters followed by fractional distillation (Blaizot—*U. S. 2,741,644*) has been patented.

Degumming soap stock was hydrolyzed with mineral acids or by autoclaving with water and centrifuged to yield fatty acids and a mixture of phosphatides, sterol glycosides and other products (Clayton—U. S. *2,758,122*). Inositol was recovered from phosphatides by liberation with caustic, extraction with alcohol and then with water (Perlman & Mattikow—*U. S. 2,746,957*).

The unsaponifiable material of foots obtained from refining cod liver oil was distilled under vacuum to obtain a cholesterol concentrate (Sone—*Japan 6882-*'54). Cholesterol was obtained from cuttle fish oil by separation and distillation of the unsaponifiable material (Imai—*Japan 227-*'55), and by converting the whole oil to methyl esters and distilling (Marumo *et al.—Japan 979-*'55; Miller & Berry—*U. S. 2,729,655–6*). In these methods the sterols were further concentrated by fractionation or crystallization from solvent, and in one case (M. & B.) it was suggested that they may be converted to complexes with acids or salts before the final solvent fractionation. Garlinskaya (*Priklad. Khim 28,* 87) has shown that chloride salts of zinc, manganese, magnesium, nickel, iron, potassium, and calcium precipitate cholesterol from an acetone solution. Calcium chloride precipitation was employed as a basis for isolating cholesterol and purifying wool fat alcohol.

Still bottom pitches and residues from distillation of vegetable oil foots were mixed with lime, dried, pulverized and extracted with alcohol to produce sitosterol concentrates which were then processed to pure sitosterols (Laquer—*U. S. 2,772,297*). The history, properties, and uses of perhydrosqualene, a product of hydrogenation of the squalene derived from fatty oils, were reviewed (Sabetay—*Rev. franc. corps gras 3,* 26).

WINTERIZING, SPLITTING, AND FRACTIONATION. Several means for winterizing or fractionating glycerides were described. The methods described for crystallizing the most saturated components from solvents made use of hexane (Varenga—*Olearia 9,* 254) and dichloroethane (Loury—*Rev. franc. corps gras 3,* 30) as solvents. Trimyristin was prepared from ucuhuba fat by crystallization from acetone (Coutinho—*Rev. brasil farm. 35,* 261).

Joshi *et al.* (*J. Applied Chem. 6,* 205) developed equilibrium curves of linseed oil-furfural-hexane mixtures at 15, 25, and 35° to serve as fundamental data for the solvent segregation of this oil. They obtained a fraction (16%) from linseed oil with an iodine value of 209. Their similar data (*Ibid.* 281) on safflower oil showed that this oil could not be fractionated by the method, presumably because of the absence of linoleno-type glycerides in the oil. This same system was used to fractionate castor oil to yield a fraction rich in methyl ricinoleate (Kasturirangan & Laddha—*J. Madras Univ. 25B,* 213). Experiments with the segregation system based on dissolving in alcohol and cooling to permit separation in phases rich in saturated and unsaturated glycerides, respectively, were unsuccessful with mowrah oil (Nath & Saha—*Indian Soap J. 21,* 125) and safflower oil (Mehta *et al.—Ibid. 20,* 289), but with linseed oil, fractions with iodine value as high as 207.7 were prepared (Mehta *et al.—Ibid.*). Twenty-two phase diagram charts of solutions of various vegetable oils, fish oils, and fats in methanol, ethanol, and ethyl acetate were prepared as fundamental data for solvent fractionation by cooling to separate fractions from solvent (Martinez-Moreno—*Anales univ. Hispalense 15,* 19).

A cosmetic-grade lanolin oil, suitable for blending with mineral oil, is obtained by dissolving wool grease in hydrocarbon solvent and a ketone followed by cooling to precipitate-out certain liquid components (Sunde—*U. S. 2,758,125*). The oil product recovered from the solvent has a cloud point of 62-7°F.

Esters of different degrees of unsaturation were also separated from fats by urea precipitation (Nakamura *et al.—Japan 8287-*'54) and by washing out with aqueous detergent solutions (Henkle & Cie—*Brit, 743,166*).

Data useful for applying the Twitchell splitting process was published on the kinetics of the reaction with babassu and cottonseed oils (Ventura—*Anais assoc. quim. Brasil 11,* 187) and on the effect of amount of reagent, washing with sulfuric acid, and heating in the splitting of soybean and rapeseed oils (Nishizawa *et al.—J. Chem. Soc. Japan, Ind. Sect. 58,* 578). A test of many splitting catalysts on cottonseed oil suggested the following descending order of effectiveness: α-naphthol, β-naphthol, *p*-cresol, *m*-cresol, cresylic acid, *o*-cresol, thymol, phenol, and *p*-nitrophenol (Wang & Wei—*Chemistry, Taiwan, 1955,* 113). A process said to yield 97-8% recovery of fatty acids was based on using zinc oxide or zinc soap as the catalyst (Antignano—*Ital. 484,620*).

Martinenghi (*Rev. franc. corps gras 2,* 773) reviewed the new processes for splitting fats by percolation. Fats were simultaneously split and increased in content of solid fatty acids by autoclaving with water and powdered selenium (Rankov & Chobanov—*Compt. rend. acad. bulgare sci. 8,* No. 2, 49). Hydrolysis of fat with some fractionation according to degree of unsaturation was accomplished by partial saponification in steps and removing the soaps after each step (Higashi *et al.—Japan 226-*'55). Another aim in this process when applied to fish oils was to separate a vitamin A concentrate, which was obtained by extracting the unsaponifiable from the filtrates with benzene.

A novel method of producing fatty acids from esters was based on dripping them through a heated column packed with glass helices (Bailey & Turek—*J. Am. Oil Chemists' Soc. 33,* 317). Even though this pyrolysis procedure gives a slightly lower yield it may be superior to saponification because: no reagents are necessary; much less time is required for reaction and purification; and the apparatus is well adapted for preparation of large amounts of acids.

Several papers appeared which were of general interest for fractionation of fatty acids. Lee (*Chem. Eng. 63,* No. 7, 189) described distillation processes and equipment for purifying fatty acid mixtures. Fichoux (*Rev. franc. corps gras 3,* 504) discussed fatty distillation with respect to number and size of plates, heating, control, etc, with special reference to distillation of tall oil and also described solvent fractionation methods. Sisley & Vallee (*Ibid.* 577) reviewed fatty and rosin acids with regard to grades, products, derivatives, uses, and research. Marin-Górriz *et al.* (*Anales real soc. espan. fis. y quim. 52B,* 73 77) demonstrated the use of certain mathematical equations in calculating the rates of evaporation of stearic, oleic, palmitic, myristic, and lauric acids in a molecular distillation processs. Molecular distillation work on Indian vegetable oils has shown that odorous compounds, free fatty acids, and unsaponifiable matter could be eliminated in the first few fractions, sesamin could be isolated from sesame oil, karanjin and pogamol could be separated from karanja oil, and with malkanguni oil there is some fractionation of glycerides (Bhat *et al.—J.Am. Oil Chemists' Soc. 33,* 197-9).

Tests on separation of solid and liquid fatty acids of tallow by crystallization in dichlorethane has demonstrated that a solid fraction of iodine value 5.9 is obtainable at 9:1 ratio of solvent to tallow and crystallization at −20° for 24 hours (Loury *et al.—Rev. franc. corps gras 3,* 30). Two recrystallizations of rapeseed oil fatty acids from 80% ethanol permitted isolation of pure erucic acid (Hadorn & Biefer—*Mitt. Lebensm. Hyg. 47,* 84). A patented method of production of stearic acid from crude technical fats was based on controlled crystallization and separating by filtration, centrifuging, or settling (N. V. Koninklijke Stearine Kaarsenfab. Gouda-Apollo—*Dutch 78,617*). Another patented method depended on the liquid fatty acids being more dispersible in aqueous solutions containing surface-active substances (Henkel & Cie—*Brit. 742,354*). Saturated fatty acids segregated from technical fatty acids were made heat and light stable by gradually adding to molten caustic under an inert atmosphere and recovering the fatty acids with mineral acid (Logan *et al.—U. S. 2,727,916*).

Other published methods of segregating fatty acids were by precipitation with urea. Tests on the effect of concentration of aqueous urea solutions and temperature of precipitation on removing saturated acids from mixed soybean fatty acids has shown that results were the same from a temperature of 5° through 30° (Sakurai & Fujiwara—*J. Chem. Soc. Japan, Ind. Sect. 59,* 33). Linoleic acid-urea complex when mixed with stearic acid or methyl stearate in benzene solution undergoes some exchange between linoleic acid and stearic acid into the complex, especially in presence of moisture (Sakurai—*J. Japan Oil Chemists' Soc. 4,* 318). Experiences on segregating fatty acids from several oils with solid urea and urea in alcohols has indicated that these methods give better results than segregating the acids by fractional crystallization as the amides (Achaya *et al.—J. Sci. Ind. Res., India, 14B,* 348). Low temperature crystallization was more efficient than urea adduct segregation methods but the latter was simpler to carry out (Chakrabarty & Biswas—*Indian Soap J. 21,* 18). Ricinoleic acid was isolated from the fatty acids of castor oil in 98% purity by urea adduct technique (Mehta & Rao—*Ibid. 20,* 119). Operation of urea adduct technique in ligroine solution was patented (Imai—*Japan 885-6-*'55). Equipment and a system were designed for use of urea or thiourea for fatty acid segregation (Huddleston—*U. S. 2,673,637*).

HARDENING OILS. New equipment and methods for hydrogenation were patented. New continuous hydrogenation involved proportioning catalyst and oil and passing through a pressure and thermal zone with hydrogen (DeNora & Bartholomaeis—*U. S. 2,750,263, 2,750,429*; Bollens—*U. S. 2,762,819*). Another continuous installation comprised a battery of consecutively joined heated autoclaves and means to transfer the substance and catalyst from one autoclave to the next (Sergeev *et al.—U.S.S.R. 103,217*). This system was also demonstrated with data from the hydrogenation of rapeseed oil (Zharskii—*Masloboino-Zhirovaya Prom. 21,* No. 3, 19). A hydrogenation vessel was equipped with a wire coil and direct current at 50 volts and one ampere was passed through it during hydrogenation to cause rapid motion of the catalyst (Itakura—*Japan 1079-*'55). A control method for measuring the progress of hydrogenation was dependent on difference between the permittivity of the substance at beginning and during the hydrogenation (Goldsmith—*U. S. 2,766,265*). Development of hydrogenation odors were inhibited by blanketing the oil to be hydrogenated with inert gas after deodorization until hydrogenation (Brown & Merker—*U. S. 2,773,081; J. Am. Oil Chemists' Soc. 33,* 141).

Several studies were made on the kinetics of hydrogenation. Vandenheuvel (*J. Am. Oil Chemists' Soc. 33,* 347, 531) reported that hydrogenation of methyl oleate in ethanol with Raney nickel was a first order reaction and that methyl stearate does not affect this rate of reaction. With platinum catalyst the product was absorbed on the catalyst and reduced the rate. His mechanism for hydrogenation of oleate with nickel catalyst was designed to include reactions resulting in the formation of *trans* isomers. Boelhouwer *et al.* (*J. Am. Oil Chemists' Soc. 33,* 143) in a study on the selectivity of hydrogenation of the ester and the intermediate monounsaturated ester; then demonstrated the equations in interpreting the hydrogenation of linseed, soybean, and peanut oils.

Allen (*J. Am. Oil Chemists' Soc. 33,* 301) and Allen & Kiess (*Ibid.* 355, 419) studied the isomerization reactions occurring during the hydrogenation of methyl *cis*-10, *cis*-12-octadecadienoate, methyl linoleate and methyl eleostearate. With addition of one mole of hydrogen, 1-2, 1-4, and 3-4 additions in the positions of the diene system occurred with equal ease to produce an equimolar mixture of *cis*-10, *trans*-11, and *cis*-12 octadecenoates. The isomerization that took place in the tests with linoleate produced *cis* and *trans*-9, -10, -11, and -12 monoenes; the double bond at the 12-position was hydrogenated slightly faster than that at the 9 position; and more octadecenoic acids with double bonds at 10- or 11-positions were produced during selective hydrogenation. The hydrogenation of eleostearate was stepwise with addition of two moles of hydrogen to the conjugated triene to produce equimolar amounts of 9-, 10-, 11-, 12-, and 13-octadecenoates. Evidence for a *cis*-9, *trans*-11, *trans*-13 structure for eleostearate was presented. Hydrogenation of sodium linoleate with Raney nickel catalyst was unselective, for even though carried out at room temperature some saturated acid was produced in the initial stages (Hashimoto—*Repts. Govt. Chem. Ind. Res. Inst., Tokyo 51,* 235). Confirmation of *trans* configuration of elaidic and isolinoleic acids separated from hydrogenated fats was obtained by infrared spectra analysis (Patil & Magar—*J. Sci. Ind. Res., India 15B,* 293).

Analyses by Elovich (*Akad. Nauk Kazakh. S. S. R. Trudy Konf. 1955,* 204) has shown that the hydrogenation of cottonseed oil is attended with interesterification among the various triglycerides in a manner such that the product approaches randomness of distribution of the various fatty acids in the glycerides. The effect of operation variables on the hydrogenation of cottonseed oil was reviewed (Eldib—*Univ. Microfilms, Ann Arbor, Mich., No. 15449,* 112 pp.).

Isanic acid which contains one double and two triple bonds was gradually hydrogenated and the changes in composition; i.e., saturated, poly double bonds, monoacetylenic, and diacetylenic acids were plotted (Seher—*Fette-Seifen-Anstrichmittel 57,* 1031).

Several communications were written on oil hydrogenation catalyst. Sultanov (*Akad. Nauk Kazakh. S. S. R. Trudy Konf. 1955,* 79) related the activity of nickel catalyst to the amount of hydrogen it could adsorb and discussed this property with relation to the effect of pressure, temperature, and presence of other metals. In an electron-microscopic study of nickel catalysts Elovich & Tretyakov (*Ibid.* 218) related activity to surface area and porosity of the metal. Directions for production and regeneration of a catalyst produced from nickel formate were issued by Gorniak (*Przemysl Spozywczy 10,* 169). Catalyst made of nickel adsorbed on sodium zeolite powder (Kodaire *et al.*—*Japan 336-*'55) and on sodium silicate (Takumi—*Japan 7012-*'54) were patented. Details were published for making nickel-alumina catalyst (Yamanaka—*J. Sci. Res. Inst., Tokyo 49,* 243), nickel-chromium catalyst without support (Sokol'skii—*Akad. Nauk Kazakh. S.S.R. Trudy Konf. 1955,* 193), nickel-copper-graphite catalyst (Okada—*Japan 8033-*'54), plain nickel-copper catalyst (Ueno—*Japan 8431-*'54), and cadmium-copper chromite catalyst (Lauer *et al.*—*Osterr. Chem.-Ztg. 56,* 255). Most of these were demonstrated with data obtained from sample hydrogenations.

Experiments on hydrogenating of oleic acid with hydrazine have demonstrated that 93% of the original oleic acid can be converted to stearic acid at 50° in six hours with agitation of the solution (Aylward & Rao—*Applied Chem. 6,* 248). Saturated fatty acids obtained from coconut fatty acids were purified of minor amounts of unsaturated acids by halogenating to reduce the iodine value below 1.0 and vacuum distilling (Hickman & Harris—*U. S. 2,748,151*).

A patented catalyst for hardening oils by isomerization was nickel on silica material which was reduced from a nickel salt in the presence of sulfur, selenium, or tellurium compounds (Unilever N.V.—*Dutch 79,307;* Mikusch-Buchberg—*U. S. 2,746,979*). Elaidinization of ricinoleic acid with selenium yielded twice as much ricinelaidic acid (24-31%) than obtained with sulfur as the catalyst (Rankov & Iovchev—*Compt. rend. acad. bulgare sci. 8,* No. 2, 41). In either case the elaidinization is hindered, possibly because of estolidation. In a test of nitrogen oxides for elaidinization of oleates, nitrogen dioxide was effective, whereas nitric oxide and nitrous oxide were inactive (Kahn—*J. Chem. Phys. 23,* 2447). A mechanism for the observation was proposed. Ethyl nitrite at high concentrations (10%) catalyzed the elaidinization of oleic acid, but with the high concentration of catalyst some addition products were formed (Rankov & Popov—*Compt. rend. acad. bulgare sci. 8,* No. 2, 37). Experiments on elaidinization of sunflower and olive oils by Angelescu & Esanu (*Acad. rep. populare Romane, Bul. stiint 4,* 359) have shown that the process did not change the properties in regard to crystallization from acetone or solubility in furfural, except when addition products of oil with selenium developed. Catalyst addition products occurred with sunflower oil but not with olive oil.

TRANS- AND INTERESTERIFICATION, PREPARATION OF PARTIAL GLYCERIDES, AND ALCOHOLYSIS OF FATS AND OILS. A process for catalytic interesterification of fats with alkali metal hydroxide without excessive saponification comprised adding the lye to a hot solution of the fat and subjecting to vacuum to reduce the moisture content to 0.01% or less (Holman *et al.*—*U. S. 2,738,278*). The spent catalyst and undesirable side products were removed from interesterified lard in a continuous process by adding hot water passing through a zone heated at 160–180°F. to break the emulsion; and the aqueous phase containing hydrated soap and deactivated catalyst is separated from the modified lard (Bates *et al.*—*U. S. 2,751,304*). A newly patented catalyst for interesterification was an alloy containing 15–50% sodium and 50–85% potassium (Hawley & Dobson—*U. S. 2,732,251; J. Am. Oil Chemists' Soc. 33,* 29). Herb *et al.* (*Ibid. 189*) prepared microscopic photographs with polarized light and phase contrast to show the difference in crystal structures of normal lard and "rearranged lard." Lard was improved for certain culinary purposes by heating at 120–260° for 0.5–6 hours in the presence of an inert gas (Norris & Mattil—*U. S. 2,763,555*). The process modifies the crystal structure without substantially interesterifying the lard.

Demarcq (*Rev. franc. corps gras 3,* 336) compared monoglyceride yields obtainable by glycerolysis of triglycerides or by partial esterification of fatty acids as influenced by catalyst, quantity of reagents, and temperature. The best but uneconomical yields were obtained with pyridine as the solvent; but butanol as a solvent with sodium alcoholates as catalyst gave only slightly inferior yields; and practically equal yields could be produced with diacetone-alcohol solvent which, however, had poor stability. Monoglycerides were formed in 70–80% yields by reacting glycerol and fatty acids in dioxane using a basic metal soap as the alcoholysis catalyst (Brokaw & van Graafeiland—*U. S. 2,732,387*).

Mono-, di-, or triglycerides were separated into fractions of uniform chemical and physical properties by fractionation in a ketone by a process in which the hot solutions are cooled to form two liquid phases containing fractions of relatively higher and lower saturation, respectively (Young & Black—*U. S. 2,740,799*). Monoglycerides were concentrated from reaction products containing 35–60% monoglycerides by extraction with aqueous methanol containing about 10% water to separate triglycerides, followed by extraction with methanol containing 30–60% water to remove most of the diglycerides (Kuhrt & Welch—*U. S. 2,727,913*). Ternary equilibrium data were obtained at 60° for mono- and dilaurin, and di- and trilaurin with aqueous ethanol and graphically presented as basic information for segregating these (Monick & Treybal—*J. Am. Oil Chemists' Soc. 33,* 193). The results served for the development of continuous countercurrent extraction process for commercial monoglycerides using 40% aqueous ethanol solution in a 4-stage agitated column. Crude monoglycerides when dissolved in 10 parts of liquefied normal gaseous hydrocarbon and cooled to 65° separate into a monoglyceride layer and another containing impurities, free fatty acids, and diglycerides (Miller—*U. S. 2,759,954*). Other methods of purifying and concentrating monoglycerides made use of urea adduct technique for the purpose (Martinez-Moreno *et al.*—*Grasas y aceites, Spain 7,* 147; Mazuelos-Vela & Vazquez-Roncero—*Ibid. 6,* 230; Rigamonti *et al.*—*Olearia 9,* 247; Aylward & Wood—*Nature 177,* 146). In a mixture of 1- and 2-monopalmitin in ether solution, powdered urea precipitated the 1-monopalmitin, whereas the 2-isomers did not form urea inclusion compounds (Aylward & Wood—*Chemistry & Industry 1956,* 53). In a test on purification of monostearin by slow crystallization with urea in methanol over 17 hours, the product isolated contained about 34% monostearin and the rest was methyl stearate (*Ibid. 1955,* 1479). Methanolysis occurred during the process.

Ethyl morrhuate was prepared by alcoholysis of cod-liver oil in presence of sulfuric acid as the catalyst (Palestrino & Guitian—*Ion, Brazil, 15,* 478). The same reaction followed by vacuum distillation was used to prepare ethyl chaulmoograte from chaulmoogra oil (*Ibid.* 425). Details were also published for producing methyl linoleate from safflower oil (Parker *et al.*—*Biochem. Preparations 4,* 86).

The influence of catalyst, temperature and time on the glycerolysis of tall oil were determined (Aries & Wolkstein—*Tappi 38,* 691). Generally the fatty acids esterified first and at a lower temperature than the rosin acids; optimum temperature for esterification was 275°, and at above 300° partial decomposition took place.

In alcoholysis of glycerides, improved yields were obtained by reaction in an inert liquid which was a solvent for the glyceride and the alcohol but was immiscible with glycerol (Coates *et al.*—*Brit. 748,401*). In a comparison of existing catalysts for the reaction, sodium methylate and ignited potassium carbonate set free 99–99.5% of the glycerol with the least production of soap from saponification by the catalyst (Hartman—*J. Am. Oil Chemists' Soc. 33,* 129). A continuous process of alcoholysis of fats and oils involved passing the reaction mixture through a reaction zone under pressure, flashing off unreacted alcohol and distillation to separate remaining fatty acids (Braconier—*U. S. 2,759,955;* Francois *et al.*—*U. S. 2,727,049*).

Products (Excepting Detergents)

HOUSEHOLD, PHARMACEUTICAL, AND COSMETIC FAT PRODUCTS. A butter product prepared from butter oil by hydrogenation to an iodine value of 20 and reconstituted with skim milk, retained an acceptable flavor for about 130 days in storage at —17°, whereas a normal butter control was unsatisfactory after one month (Weihe—*J. Dairy Sci. 39,* 910). The manufacture of a simulated butter by interesterification of a selection of fats whose combined fatty acid mixture contains 77% C_{12} to C_{18} acids with the remainder composed of small amounts of C_6, C_8, C_{10}, and C_{20} acids was patented (Cochran & McGee—*U. S. 2,726,158*).

A margarine made by adding part of the salt and milk to the fat, cooling until partly crystallized, followed by adding the remainder of the salt and milk blend and chilling, had a much lower capillary slip melting point than margarine in which all the aqueous portion was added initially (Shafer *et al.*—*U. S. 2,745,750;* Schmidt & Schafer—*U. S. 2,772,976*). A margarine mix cooled to the point of microcrystal formation and tempered for 3–48 hours resisted melting on hot days (Jones & Lancaster—*U. S. 2,754,213*). Margarines and butters were prepared in dry powdered form by spray drying the emulsions (Kosin & Khomutov—*Masloboino-Zhirovaya Prom. 21,* No. 5, 21). In this work the lactose of the milk ingredient was replaced with sucrose to eliminate formation of both volatile and nonvolatile unsuitable substances by reaction of lactose with casein during storage. Tests on storability of wrapped German margarines have shown that aluminum foils gave best protection against autoxidation and loss of moisture (Schmidt—*Fette-Seifen-Anstrichmittel 58,* 821).

Fritter and French-fried potato frying tests were made using steam-rendered and continuous-process lard, cottonseed oil, peanut oil, and two blended shortenings containing molecular-modified lard mixed with other fats, an antioxidant mixture, and mono- and diglycerides (Bennion & Hanning—*Food Tech. 10,* 229, 290). The continuous process lard appeared superior to steam rendered lard in regard to maintaining a high smoke point and low fatty acids. The addition of monoglycerides to lard lowered the smoke point and did not influence fat absorption by the food. Antioxidants had some effect on peroxide values, but none on smoke point or free fatty acid development. Palatability and odor tests by panel judges did not distinguish between fritters fried in fresh or greatly used fats. The color changes of various fats used in frying the fritters were similar for each product fried but varied according to the flour mixture being fried. Deep fat fryers in which the frying fat was continuously circulated through a filter (Mies—*U. S. 2,760,645*), and a deaerator (Smith—*U. S. 2,767,095*), respectively, were patented.

Consistency measurement data were developed for use as a basis for making blended shortening from cottonseed and mbocaya oils (Landmann & Feuge—*J. Am. Oil Chemists' Soc. 33,* 308). Tallow, when slightly hydrogenated and stabilized with antioxidants produced suitable shortenings when blended with cottonseed oil (Morris *et al.*—*Ibid.* 353). New patents on plastic shortenings pertained to: continuous methods for adding emulsifier and tempering lard (Griffin *et al.*—*U. S. 2,728,674–5;* Johnson—*U. S. 2,770,544*), a lard containing partial ester compounds and cholesterol-free lipides extracted from animal brains and spinal cords (Kiers—*U. S. 2,733,149*), and a product containing polyoxyethylene ether of a solid partial fatty acid ester of a hexitan (Cross & Griffin—*U. S. 2,746,868*). Fatty acid esters of lactylic acid, when added to shortening or to the yeast leavened baked products, act as plasticizers, emulsifiers, and biologically active agents which improve the appearance of baked products and inhibit staling (Thompson & Buddemeyer—*U. S. 2,733,252, U. S. 2,744,825–6*). Details for using calcium stearyl 2-lactylate in baking bread and the effect of variables on the final product have been worked out (Bechtel *et al.*—*Cereal Chem. 33,* 206). The shortening product of India, vanaspati, was fortified with synthetic vitamin A palmitate and investigated for loss of vitamin during storage and cooking (Chitre & Khale—*J. Sci. Ind. Res., India, 15C,* 74, 77). The samples tested lost 25% of the added vitamin in six weeks in open containers or six months sealed, and 20% loss occurred on heating at 95° for 20 minutes.

X-ray photographs and moisture contents were recorded for flour-moisture-salt-yeast breads to which 4% of various shortening and emulsifiers had been added (van der Lee & Weibenga—*Brot u. Gebäck 9,* 135). The x-rays indicated a progressive change, like a crystallization of the starch during storage, which was most effectively retarded with use of the emulsifiers, glycerol monostearate and diacetyl tartaric acid esters of mono- and diglycerides. The importance of lipides in breadmaking was reviewed by Cookson & Coppock (*J. Sci. Food & Agr. 7,* 72). They drew particular attention to lipoprotein fractions, their extraction, effect of aging, and behavior of added shortening in bread prepared from defatted flour.

Conventional nonemulsifier and emulsifier shortenings, texturized with and without the usual 10% occluded gas content and also samples solidified by slow cooling without agitation were tested in yellow pound, yellow layer, and white layer cake formulas (Thompson & Gannon—*Cereal Chem. 33,* 181). Emulsified gas and texturization contributed to the performance in creaming cakes, but additional mixing could compensate for their absence. Optimum level of monoglyceride in shortening was 3%. One patent on a cake batter pertained to replacing part of the eggs in the formula with a foaming emulsifier and fat (Crossland & Beasly—*U. S. 2,768,082*).

Vegetable oils bodied at 20–35°F. below their flash point were patented as baking-pan greases (Hansen—*U. S. 2,758,928*). An anti-adhesion "wax" for coating inner surfaces of food containers was made by condensing fatty acids with ammonia or an amine (Edgar & Spannuth—*U. S. 2,735,354*). A powdered edible fat was made by running coconut oil at 40° through a spray drier whose drying chamber was cooled to —5° (Iguchi *et al.*—*Japan 978-'55*). Solidified chocolate products were made self sustaining above the melting point by the presence of 2–3% water in a manner to wet the surface of non-fat particles (Kempf & Downey—*U. S. 2,760,867*).

A dried dairy fat product containing 22% non-fat milk solids was made by spray drying cream and packed in vacuum cans (Shtal'berg—*Trudy Vsesoyuz. Nauch. Issledovatel. Inst. Molochnoi Prom. 1953,* No. 14, 35). The product is suitable for reconstitution to cream; or, on addition of skimmilk, to milk. Litman *et al.* (*J. Dairy Sci. 39,* 909) attributed loss of solubility in dried whole milk products to the development of a fat-protein complex, which in reconstituted milk forms an insoluble scum that clings to the walls of containers. This scum contained 48% fat which had a higher melting point and lower iodine value than the original butter fat. A milk product in which the butterfat has been replaced by vegetable fat was patented (Almeda—*Span. 217,450, 217,452*).

A newly patented mayonnaise contained about 80% olive oil (Mod. Appl. Refrig. Industrial, S.A.—*Span 217,490*). The keeping quality of cooked and roasted nut meats was enhanced by coating with glyceryl monostearate and salting (Newmann —*U. S. 2,742,364*). Wax emulsion coatings for fruits and vegetables contained oil soluble detergent as emulsifiers (Gericke—*U. S. 2,755,189*).

Several pharmaceutical materials were prepared as fat derivatives. Vitamin A palmitate was prepared from a fish-liver oil vitamin A concentrate by palmitylation with the acid chloride (Kimumaki—*Bull. Japan Soc. Sci. Fisheries 20,* 1027). A stabilized powdered vitamin A preparation contained vitamin A palmitate, gentisic aldehyde, fatty amine, lecithin, and tocopherol adsorbed on magnesium oxide (Kläui—*U. S. 2,764,520*). Another dry free-flowing fat-soluble vitamin powder was made by dropping vitamin-gelatin emulsion on a starchy powder (Cannalonga & Magid—*U. S. 2,756,177*). Fatty acid derivatives of pantothenic acid were synthesized and found to be equal in activity to the free pantothenol (Sakuragi & Kummerow—*J. Am. Chem. Soc. 78,* 838; *J. Nutr. 59,* 327). Esterification of free pyridoxine (vitamin B_6) with a palmitoyl group induced a marked improvement in the heat stability of the vitamin and reduced its susceptibility to destruction by the intestinal flora (Sakuragi & Kummerow—*J. Am. Oil Chemists' Soc. 33,* 116; *J. Am. Chem. Soc. 78,* 839;

Arch. Biochem. & Biophys. 63, 32; *J. Nutr. 58,* 557). In two of three separate trials involving a total of 145 pigs the addition of trimethylalkylammonium stearate to the ration significantly stimulated growth (Lueche *et al.*—*J. Animal Sci. 15,* 765). Quaternary salts containing fatty radicals were used as solubilizing agents for the antibiotics, gramicidin and subtilin (Nepera Chem. Co.—*Brit. 735,672*). A hexylresorcinol therapeutic agent was prepared as a solution in castor oil (Boskamp—*U. S. 2,775,538*).

Ricinoleate compounds inhibited flavobacterium (Venkataraman & Sreenivasan—*Current Sci., India 25,* 190). Both fresh and autoxidized calamary fish oil inhibited growth of many types of bacteria (Tomiyasu & Toyomizu—*Bull. Japan Soc. Sci. Fisheries 21,* 253). Free saturated acids of 10–16 carbon atoms and their salts with alkaline earth metals showed *in vitro* bacteriastatic power against *Mycobacterium tuberculosis* (Hirsch & Barchet—*Deut. Z. Verdauungs-u. Stoffwechselkrankh. 15,* 214).

Penicillin yields in 50-gallon fermentors were increased from 1400 to over 2000 units per ml. by adding lard to the fermentation at intervals throughout the run (Anderson *et al.*—*J. Agr. & Food Chem. 4,* 556).

Two reviews were written on uses for fat and fat derivatives in cosmetics (Velon—*Rev. franc. corps gras 3,* 587; Babayan—*J. Soc. Cosmetic Chemists 7,* 225). A patented lipstick contained dye, fatty esters of dextran, fatty acids, and wax (Novak & Tyree—*U. S. 2,749,276*). A water-in-oil-type toilet cream formula contained polyvinyl alcohol, turkey red oil, sorbitan sesquipalmitate and silicone oil (Saigo—*Japan 1250-'55*). A mixture of completely and partially hydrogenated cottonseed oil was said to be superior to other bases for fat-type suppositories (Hartman & LaRocca—*J. Am. Pharm. Assoc. 45,* 86). Many commercial nonionic surfactants were evaluated with regard to releasing medication from hydrophilic ointment bases (Barker *et al.*—*J. Am. Pharm. Assoc. 45,* 527).

A brief review of processing fats for special purposes, such as shortening, candy making, synthetic cream, etc., was prepared by Paterson (*Food Manuf. 31,* 386).

EMULSIFIERS AND DEMULSIFIERS. Several communications were of general interest in regard to emulsification and use of emulsifiers. Isemura (*J. Chem. Soc. Japan Ind. Sect. 58,* 815) wrote a review on the subject. In England a "permitted list" of emulsifiers for use in food was issued (anon.—*Food Manuf. 31,* 466; *Food 25,* 405). Data on the rheological properties of lecithin and its mixtures with soybean oil were recorded by Jancik (*Prumysl Potravin 7,* 33). Cockbain (*J. Colloid Sci. 11,* 575) measured the adsorption of serum albumin and sodium sulfate at emulsion interfaces. The emulsifier formed a complex with the albumin. Conditions under which the complex is displaced from the interface by excess dodecyl sulfate are described. Fieser *et al.* (*J. Am. Chem. Soc. 78,* 2825) prepared numerous synthetic emulsifying agents containing fatty, sugar, and amino groups and their emulsifying properties were examined. Conjugates of various amino acids with stearylamine appeared to have promising emulsifying properties. Surface active monoesters were prepared from fatty acids and sucrose (Osipow *et al.*—*Ind. Eng. Chem. 48,* 1459, 1462). Because of nontoxicity these should be particularly useful in cosmetic, pharmaceutical, and food applications. Methyl glucoside and glucose were partially esterified by palmitic acid (Asselineau—*Bull. soc. chim., France 1955,* 937).

A comprehensive investigation of monoglyceride emulsifiers has shown that: monolaurin and monomyristin lowered surface tension most; with water-oil systems the effectiveness of the emulsifier in lowering the interfacial tension was poorer as the chain length of the fatty acids of the oil decreased; and the greater the interfacial tension of water-organic compound systems the greater was the effect of the emulsifier (Tsuda & Wada—*Repts. Ind. Res. Inst. Osaka Prefect. 7,* 45). The alcohol soluble moiety of vegetable lecithin has a synergistic effect on mono- and diglyceride emulsifiers (Julian *et al.*—*U. S. 2,773,771*).

New patents have been issued on emulsifier compounds containing fatty acid, polyoxyethylene, and sugar radicals (Barker—*U. S. 2,753,303;* Hall—*U. S. 2,761,784;* Hällqvist & Hellving—*Swed. 151,064*). Such emulsifiers were recommended to facilitate the solution of essential oils (Breinlich—*Krankenhaus-Apoth. 6,* 9). Lower & Cressey (*Food Manuf. 31,* 277) point out that such compounds render the baker's task easier and his product more attractive and concludes that if unobjectionable they should be used. A group of investigators have found polyoxyethylene derivatives toxic and have listed eight abnormal pathological and other changes resulting from feeding the preparations to rats and hamsters (Poling *et al.*—*Food Res. 21,* 337; Eagle *et al.*—*Ibid.* 348). Results from other investigations have indicated that these compounds are innocuous when administered in amounts equivalent to those that may be commercially added to foods or used in pharmaceuticals (Wick & Joseph—*Ibid.* 250; Kruesi & Van Itallie—*Ibid.* 565; Oser & Oser—*J. Nutr. 60,* 367). Polyoxyethylene derivatives of polymerized oils were definitely toxic (Aes-Jorgensen *et al.*—*Brit. J. Nutr. 10,* 32).

History, statistics, properties desired, and future of using soap as an emulsifier in synthetic-rubber manufacture were reviewed (Druesdow—*Soap & Chem. Specialties 32,* No. 4, 41). One patent pertained to a novel method for using soap in the process (Davison & Dunn—*Can. 511,371*). In a process for making latex-foam-sponge the soap foaming agent was improved for the purpose by the presence of a salt of perfluoromonocaprylic acid (Eckert—*U. S. 2,761,001*). A decrease in stability of ammoniated and soap-stabilized latex emulsions in the presence of zinc oxide was attributed to hydration of the compound, zinc diamine dilaurate, formed at the surface of the rubber or oil particles (McRoberts—*Proc. 3rd Rubber Tech. Conf., London 1954,* 38). An investigation of the relation of the structure of alkyl aromatic sulfonic acid type emulsifiers and synthetic rubber polymerization has indicated that naphthalene derivatives were better than benzene derivatives, and solubilization increased from the mono- to trialkyl derivatives (Apukhtina & Lyagalova—*Kolloid Zhur. 17,* 337). A mixture of potassium soap, alkyl aryl sulfonate and formaldehyde (Williams & Fordham—*U. S. 2,753,327*), and special soaps of tall oil and naphthenic acids (Hetzel—*U. S. 2,752,330*) were patented for emulsion polymerization of butadiene products. Also patented for the same purpose were certain paraffin sulfonates prepared by saponifying sulfochlorinated paraffins (Quaedvlieg—*Ger. 902,614*).

Formulas developed for fungicides (Elliot & Nicholson—*U. S. 2,756,233*), insecticides (Swarbruck—*U. S. 2,765,255*), and molluscacides (Johnson & Todd—*J. Parasitol. 41,* 553) contained emulsifiers or wetting agents. A resin coating for grease proofing paper contained a fat derived nonionic emulsifier as a dispersing agent (Brown—*U. S. 2,757,106*). Fatty or rosin acid salts of *N*-dialkylamino alkylamines (Jelling—*U. S. 2,737,509*) and reaction product of ebony fat and tetramethylenediamine (Kalinowski & Crews—*U. S. 2,772,179*) improved adherence of bituminous emulsions to damp mineral aggregates.

Condensation products of discarded hot dip tinning palm oil and alkylene oxide are useful as petroleum demulsifiers (Case—*U. S. 2,745,855*). An emulsion for fracturing underground formation by pressure in petroleum production contained kerosene, moisture, calcium chloride, emulsifier (Tween-20) and diethyl amine (Brainerd—*U. S. 2,742,426*). In one field test, little definite increase in oil-production rate or lessening of normal production-decline rate was observed as a result of detergent injection (Dunning *et al.*—*Producers Monthly 20,* No. 5, 29).

ESTERS, ACIDS, ALCOHOLS, AND OTHER FAT DERIVATIVES. Interest has continued in "acetin" fats which are made by interesterifying triacetin with natural glycerides. They had been suggested for use in the food and pharmaceutical industry and technically as plasticizers, lubricants, wax coatings, etc. Lashkari (*Bombay Tech. 6,* 61) reviewed their synthesis, properties and uses. New products of this type were made by interesterification of glycerol, triacetin, and lard (Embree—*U. S. 2,764,605*) and by acetylating monoglycerides (Feuge *et al.*—*U. S. 2,745,749*). Their absorption and digestibility are good (Ambrose & Robbins—*J. Nutr. 58,* 113), and it has been demonstrated that they are nontoxic (Ambrose & Robbins—*J. Am. Pharm. Assoc. 45,* 282; Mattson *et al.*—*J. Nutr. 59,* 277). In the interest of using acetostearin products as protective coatings for food products their permeability to carbon dioxide, oxygen, and nitrogen has been determined and compared to that of other coating and wrapping materials, (Lovegren & Feuge—*J. Agr. Food Chem. 4,* 634).

The hydroxy groups of hydroxy fatty acids having conjugated double bonds, as α- and β-kamololenic, and 12- and 9,10-dihydroxystearic acids, can be quantitatively acetylated at 27–32° with acetyl chloride in ether solution (Pathak & Aggarwal—*J. Sci. Ind. Res., India, 14B,* 637). Esters of cinnamyl alcohol with several fatty acids were prepared by reaction with the acid chlorides in pyridine solution (Gonella & Abbattista—*Gazz. chim. ital. 85,* 561). By using the greater reactivity of primary hydroxyl groups of glycerol and the solvent action of dimethylformamide pure symmetrical 1,3-diglyceride was prepared by alkylation with the acid chloride and the synthesis was extended to obtain pure triglyceride of known structure (Hartman—*Nature 176,* 1024). Pure L-ω-(dioleyl) lecithin was synthesized and its characteristics were determined (Baer *et al.—J. Am. Chem. Soc. 78,* 232). Fourteen fatty esters of cholesterol were prepared and their melting points and mesomorphic transition temperatures recorded (Gray—*J. Chem. Soc. 1956,* 3733).

In fundamental investigations several fatty acids were synthesized. Linolenic acid was prepared for use to confirm the structure of the natural acid (Nigam & Weedon—*Chemistry & Industry 1955,* 1555; *J. Chem. Soc. 1956,* 4049). Oleic acid was prepared by anodic synthesis from acetylenic components (Baker *et al.—J. Chem. Soc. 1955,* 2218). Other fatty acids that were synthesized for fundamental purposes are: chaulmoogric (Mislow & Steinberg—*J. Am. Chem. Soc. 77,* 3807), stearolic (Khan—*J. Am. Oil Chemists' Soc. 33,* 219), *dl*-11-methyllauric, arachidic, *dl*-tuberculostearic (Sy *et al.—Compt. rend. 239,* 1813), pentadecanoic, nonadecanoic, doconsanic (Bergmann & Ish-Shalom—*Bull. Res. Council Israel 5A,* 65), and many branched chain higher fatty acids (Bailey *et al.—J. Chem. Soc. 1955,* 1547; Cason & Rinehart—*J. Org. Chem. 20,* 1606; Allen—*Ibid. 21,* 143; Schulte *et al.—Hoppe-Seylers' Z. physiol. Chem. 288,* 69).

Optimum conditions were determined for esterifying phenol with fatty acids using active clays as catalysts (Watanabe—*J. Chem. Soc. Japan, Ind. Sect. 57,* 579). Fatty acids were substituted in the α- or ω-, or both α- and ω-positions with phenyl groups in the preparation of compounds which were required in some biological studies (Hase & Oura—*Pharm. Bull., Japan 2,* 368). Aluminum chloride-catalyzed arylation with various aromatics at the double bond of alkyl erucates produces compounds that might be useful in preparation of high viscosity lubricants (Buu-Hoi *et al.—J. Org. Chem. 21,* 621). A study of diethyl acylphosphonates prepared by the reaction of fatty acid chlorides with triethyl phosphite has indicated that the acylphosphonate rather than an anhydride structure is correct (Ackerman *et al.—J. Am. Chem. Soc. 78,* 4444, 6025). In this work the compounds were prepared from the C_4–C_{18} saturated acids and oleic acids and their properties were recorded. Methyl α-eleostearate in acetic acid reacted with mercuric acetate at below room temperatures to yield products of high mercury content (Planck *et al.—J. Am. Oil Chemists' Soc. 33,* 350). For each mole of mercuric acetate added, one mole of mercuric acetate was reduced to mercurous acetate. When magnesium, zinc, tellurium, selenium, and several other metals were diffused into linseed oil from electrodes by electric current the metals were absorbed and the iodine number of the oil was reduced (Kubicz *et al.—Acta polon. Pharm. 13,* 139). It was said that the magnesium dispersion had healing properties for wounds.

Fatty acids were reacted with formaldehyde (Gayer—*U. S. 2,744,889;* Knight *et al.—U. S. 2,759,953*) and paraformaldehyde (Rochett—*U. S. 2,764,604*) to yield products useful for manufacture of resins, plastics, coatings, waxes, adhesives, lubricants, or dispersants, or could be hydrolyzed to hydroxy fatty acids. The catalyzed addition of formic acid to oleic acid was exclusively at the 9- and 10-positions (Rochett—*J. Am. Chem. Soc. 78,* 3191).

Dimeric acids were prepared from fatty acids containing only one double bond by heating to 100° in the presence of di-*tert.* butyl peroxide (Harrison & McCaleb—*U. S. 2,731,481*).

Studies on increasing the unsaturation of ricinoleic acid by halogenation followed by dehydrohalogenation showed good halogen saturation of the acid but on dehydrohalogenation there was poor increase in unsaturation (Rao *et al.—Indian Soap J. 20,* 201). Halogenation followed by dehydrohalogenation was successful in increasing the unsaturation of synthetic fatty acids obtained by paraffin oxidation (Nebe—*Ger. 851,184*). Results of hydroxylating methyl oleate dispersed in varying quantities of acetic acid solution with and without sulfuric acid by treatment with ammonium persulfate were tabulated (Naudet—*Ind. chim. belge 20, Spec.* No. 721). The products were mixtures of methyl oleate, methyl dihydroxystearate, methyl acetohydroxystearate, and methyl oxostearate. The hydroxylation of vegetable oils by reaction with lactic acid then with hydrogen peroxide was patented (Julian *et al.—U. S. 2,752,376*).

Oxidation of methyl oleate in the dark in presence of metal deactivators, as ascorbic, citric, or phytic acid, yielded products containing as high as 35–45% peroxides (Swern *et al.—U. S. 2,750,362*). In a study on effect of variables on ozonization of oleyl alcohol in acetic acid solution, the highest oxide content was produced at 22° (Izumi—*J. Chem. Soc., Japan, Ind. Sect. 58,* 803). Studies were also reported on oxidation of oleic acid with periodate in the presence of permanganate, giving the amounts of oxohydroxystearic, azelaic, 10-oxo-11-hydroxyundecanoic, sebacic and other acids produced under various conditions (Lemieux & Von Rudloff—*Can. J. Chem. 33,* 1701).

The epoxidation of unsaturated fatty acids in organic solvent and formic acid at 50–80° with hydrogen peroxide was patented (Greenspan & Gall—*U. S. 2,774,774*). Fatty acids, nitrites and esters were also epoxidized by preparing the formoxychloro-compounds and hydrolyzing with potassium hydroxide in ethanol solution (Riener—*U. S. 2,756,242*). Pigulevskii & Kuranova (*Zhur. Priklad, Khim 28,* 1353) epoxidized methyl oleate and methyl linoleate in ether with acetic acid and active oxygen and recorded yields. A study on the epoxidation of vinyl oleate shows that the double bond of the oleate radical is oxidized at 220 times the rate of that in the vinyl moiety (Silbert *et al.—J. Polymer Sci. 21,* 161). Natural epoxyoleic acid has been proven to be an optically active *cis*-epoxide and has been converted into erythro-12, 13-dihydroxyoleic acid and eight optically active 9-, 10-, 12-, 13-tetrahydrostearic acids (Bharucha & Gunstone—*J. Chem. Soc. 1956,* 1611). The hydrogenation of epoxidized compounds with the use of palladium on carbon as the catalyst was patented (Mack *et al.—U. S. 2,727,048*). Blaizot (*Oleagineux 10,* 311) reviewed the epoxidation and hydroxylation of fatty materials, and the industrial application of the products.

The literature on fatty alcohols includes information on natural sources and synthesis from fats by soduim reduction and by hydrogenation. A review on production, properties and uses was prepared by Hill *et al.* (*Parfums, Cosmetics, Savons 1955,* No. 115, 33). Two other communications were on wool fat, alcohols derived therefrom, their derivatives and uses (Lower—*Soap, Perfumery & Cosmetics 28, 1128,* 1260; Miyakawa—*Repts. Osaka Ind. Res. Inst. No. 304,* 116 pp.). A continuous method of sodium reduction of glycerides to alcohols made use of butylcarbinol and toluene solvent and five times the required sodium; and the unexhausted metal dispersion was recirculated to the reduction zone (Hulse & Schott—*U. S. 2,761,882*). This type of reduction was facilitated by incorporating pyridine in the reduction mixture (Wilson—*U. S. 2,748,175*). In a study of the reaction kinetics of butyric and lauric acids with sodium in benzene the equilibrium constants were found to be 6.1×10^{-6} and 1.7×10^{-7}, respectively (Gindin *et al.—Doklady Akad. Nauk S.S.S.R. 106,* 683). Data have been recorded on production of alcohols by hydrogenation of cottonseed oil using cadmium modified copper chromite catalyst (Lauer *et al.—Österr. Chem.-Ztg. 56,* 255) of coconut oil using barium-copper chromate catalyst (Matsuda & Toyoda—*J. Chem. Soc. Japan, Ind. Sect. 58,* 523) and of bagasse and grape seed oil with copper-chromium catalyst (Delgrado—*10th Congr. intern. ind. agr. y aliment Madrid 1954,* 3623). The production of octanol by hydrogenation of octyl caprylate using copper-chromite catalyst was patented (Takao & Kumamoto—*Japan 6566-'54*). High molecular weight alcohols were also prepared by passing lower molecular weight alcohols over a mixture of magnesium, aluminum and zinc at high temperatures and pressure (Querfurth—*Ger. 911,730*). Cetyl alcohol has been submitted to the Guerbet reaction and converted into 2-tetradecyloctadecal alcohol (Sulzbacker—*J. Applied Chem. 5,* 637).

Oxidation and pyrolysis were used to convert fatty material into commercially valuable fission products. Oxidation with nitric acid was used to prepare mono- and dibasic acids of shorter chain length than the original material (Ölund—*Swed. 153,086;* Engler & Richards—*U. S. 2,773,094–5*). This type process produced mainly azelaic and suberic acid from oleic acid; suberic, glutaric, and pimelic acid from linoleic. azelaic suberic, glutaric and sebacic acids from conjugated linoleic acid; and tall oil gave mainly glutaric acid (Kirjakka & Nieminen—*Suomen Kemistilehti 28B,* 9). Unsaturated acids were halogenated and then fused to yield saturated acids of shorter chain length (Walling—*U. S. 2,760,969*). A method of preparing azelaic acid involved halogenating oleic acid, dehalogenating to form dihydroxystsearic acid, and oxidizing this with chromic acid (Kobayashi & Miyazaki—*Repts. Govt. Chem. Ind. Res. Inst. Tokyo 49,* 73, 78). Applying the last of the above steps to the fatty acids derived from sperm whale oil yielded about 24% dibasic acids and 28% pelargonic acid (*Ibid.* 82). Fission products are also obtained by heating polyhydroxy fatty acids with caustic (Kessler Chem. Co.—*Brit. 731,061*). This method is used to prepare sebacic acid from castor oil (Emslie—*U. S. 2,731,495*). Ricinoleic acid was also pyrolyzed to obtain heptanal and 11-dodecenoic acid (Vierhapper & Orlicek—*Austrian 184,174*) or heptanol and undecylenic esters (Gregory & Kostelitz—*U. S. 2,737,519*). The newly published methods of segregating the dibasic acid of mixed fission products of fatty materials were based on liquid-liquid partition between aqueous and organic phases

(Higuchi—*U. S. 2,744,067*) and on fractional crystallization (Miwa & Ueno—*Japan 5520-1-'54*). A method of separating the dibasic acids for analysis depended on preparation of paper chromatographs from water-alcoholic ammonia liquor and staining with solution of ninhydrin (Seher—*Fette-Seifen-Anstrichmittel 58,* 401).

Many nitrogen derivatives of fatty acids, such as nitriles, amines, and amides, were subjects of patents and communications. Fatty acid nitriles were manufactured by reacting the acids with amines in presence of metal oxide catalyst (Soc. anon. d'innovations chim.; Sinnova ou Sadic—*Fr. 986,870*). An industrial method for preparation of 500 kg. of nitrile per day involved passing the acid with excess of ammonia gas at 360–70° over alumina catalyst (Kircher—*Bull. soc. chim. France 1955,* 455). Fatty nitriles were hydrogenated to amines by heating with hydrogen and carbon monoxide in the presence of cobalt catalyst (E. I. du Pont de Nemours & Co.—*Brit. 728,599*). The carbon monoxide was included to preserve the activity of the catalyst. Unsaturated fatty acids were converted to ω-amino acids by ozonizing the soaps of the acids and then reacting with hydroxylamine hydrochloride (Ohtsuki & Funabashi—*Japan 8417-'54*). Hecadecyl-2,5-oxaolidinedione was prepared by passing carbonyl chloride into *dl*-amino-2-stearic acid, which subsequently was converted to aggregates in benzene solution with potassium carbonate as the initiator (Parrod & Spach—*Compt. rend. 242,* 1299).

Higher fatty acid halides were condensed with salts of lower aliphatic amino monocarboxylic acids to form fatty acid amides in high yields and purities (Krems—*U. S. 2,729,657*). Amides of epoxyamines prepared by Payne & Smith (*U. S. 2,730,531*) were characterized as containing an epoxy oxygen atom linked to vicinal carbon atoms of a hydrocarbon radical which is bound directly to a nitrogen atom of a fatty amide. An x-ray investigation of normal fatty acid amides has shown that four types of crystals occur at room temperature for the C_{16} compound and three types for the C_{18} (Kurokawa—*Bull. Chem. Soc. Japan 28,* 660).

The nitration of fatty alcohol with fuming nitric acid while in acetic anhydride solution has been patented (Lane—*Brit. 713,329*). These nitrates could be converted to quaternary pyridinium nitrates. Guanidino substituted fatty acids were prepared from α-brominated fatty acid and guanidine acid salts (Garst & Vassel—*U. S. 2,766,282*).

Fatty Materials Used in Textile Sizes, Waterproofers, Wax, Defoamers, Foam Producers, Anticorrosive, Pressure Transmitting Fluids, Drilling Fluids, Incendiary Preparations, Water Insoluble Soap, and Miscellaneous Products. Fats, oils, and waxes were added to protein and starch textile sizers as softeners (Farkas—*U. S. 2,757,097*). Gelatine sizes containing oxygenated fatty acid salts were suited for most water repellent fabrics (Fraizy—*U. S. 2,735,781*). Waterlaid glass fibers were sized by an amide formed by condensing fatty acids with polyalkylenepolyamines (Landes & Reynolds—*U. S. 2,758,026*).

Textiles were waterproofed by applying a solution of chloromethyl acid amide, fatty nitrile and formaldehyde, and heating to decompose the mixture to an insoluble residue (Pingree & Stevens—*U. S. 2,750,306*), with organic solvent solutions of esters of dextran with saturated fatty acids (Novak & Tyree—*U. S. 2,766,143*), and with silicone derivatives emulsified with fatty derivatives (Gagarine & Repokis—*U. S. 2,750,305*).

A defoamer for latex emulsions comprised a mixture of stearic acid, polyoxyethylene esters of tall oil, kerosene, aluminum hydrate and monoethanolamine (Larsen & Lam—*U. S. 2,773,041*). A product for use in the manufacture of paper pulp contained paraffin hydrocarbons, monostearin, fatty alcohol-fatty acid esters and esters of polyethylene glycol with fatty acids (Snook—*U. S. 2,715,614*). The preparations patented for general defoaming uses were: a combination of sugar cane oil and a polyoxyethylene-fatty acid emulsifier (Kulakow & Kent—*U. S. 2,762,780*), a mixture of glycol ester emulsifier and mineral or fatty oil (Figdor—*U. S. 2,753,309*), and a condensation product of triethanolamine, oxyethylene groups and fatty acids (Monson—*U. S. 2,748,089*). A study of soap, detergent, and protein produced foams has suggested that outstanding foam stability is dependent on formation of plastic surface films; and that antifoaming action is related to the destruction of the surface plastic film by the defoamer (Ross & Butler—*J. Am. Chem. Soc. 60,* 1255). In another study on defoamers, equilibrium spreading pressures were measured for the C_{12} to C_{17} diacylated piperazines, and for the dipalmityl, distearyl, and dioleyl diethylene triamines (Hawke & Alexander—*J. Colloid Sci. 11,* 419).

New foam-type fire extinguisher fluids were made of a combination of sodium salt of hydrolized protein and alkylamine salts of fatty acids (Ratzer & Levine—*U. S. 2,767,141*), and by combining solutions containing stearic acid, isopropyl alcohol, chloroform, and ethanolamines with solutions containing sodium carbonate and aluminum lactate (Perri & Dollman—*U. S. 2,758,969*). The chief requirements of the surface active agents used for making light concretes have been elaborated and several laboratory prepared and commercial products have been evaluated for the purpose (Pfanner—*Silikattech. 6,* 396).

A polishing wax emulsion contained an emulsifying agent and tertiary diethanolamine salts of fatty acids in which saturated fatty acids were dominant (Fischer—*U. S. 2,772,173*). A silicone-type polishing composition included blown castor oil and an anionic sulfated fatty wetting agent among its ingredients (Kingdon—*U. S. 2,738,282*). Reaction products prepared from fatty and cycloaliphatic *p*-diamines varied from materials of wax consistency to elastic, hard products of dropping points as high as 250° (Badische Anilin & Soda Fabrik A.-G.—*Ger. 932,965, 934,767*). A liquid buffing compound contained glue, diethylene glycol, fatty grease, wax emulsifier, abrasive, and water (Candee & Doughty—*U. S. 2,765,223*).

Sperm oil intended for sulfonation for use in tanneries should be submitted to a "winterization" process to lower the melting point to —8° (Pilc—*Kozarstvi 5, 168*). An investigation of sulfonated auxiliary agents, with the aid of radio active products, in chrome leather manufacture, showed that leather takes up more emulsifier the greater the amount is used; a small amount is retained in tanning; most is retained under the grain, approximately at the hair roots; and it is possible to tan a chamois-like leather with use of alcohol sulfonates (Heyden *et al.*—*Das Leder 7,* 100). To improve the properties of fish oils for oiling lelather they were inoculated with fat splitting bacteria, and aerated until the acidity was increased to over 10% (Bruzac—*Fr. 998,607*). A review of synthetic oils prepared for replacement of the fatty oils used in leather manufacture was prepared by Das *et al.* (*Indian Soap J. 20,* 71). A photomicrographic study of the leather fat-liquoring process has shown that in nonfat-liquored leather fibers stick together, and hair follicles and interfibrillary capillaries collapse, whereas fat-liquoring separates fibers and keeps the capillaries open (Das *et al.*—*Bull. Central Leather Res. Inst. Madras 2,* 402). Fatty spue on chrome leather was investigated using stearic acid, tristearin, and sulfonated triolein in seven combinations dissolved in benzene for fat-liquoring (Mitton & Pankhurst—*Das Leder 7,* 169). Stearic acid spue occurred at high humidity and at 0°, and tristearin spue appeared at 44° and low humidity. Swabbing leather with ammonium hydroxide solution reduced spue. The spue formed because fat crystals grew at the expense of the amorphous portion of the fat.

There was some literature on using fat derivatives for flotation. Spodumene was floated with the use of sulfonated oils as the flotation agent (Bunge—*U. S. 2,748,938*). An improvement of fatty amine flotation of potassium chloride from potash ores, containing clays which adsorb the flotation agent, comprised precipitating metal hydroxides in the brine prior to addition of the fatty amine (Schoeld *et al.*—*U. S. 2,757,796*). Hydrocarbon impurities were floated from aqueous media by adding partial fatty acid esters of polyhydric alcohols and aerating (Boyd & Fischer—*U. S. 2,759,607*). An investigation on floatability of chalcopyrite in the presence of oleic acid has demonstrated that the presence of oxygen is necessary (Bessonov *et al.*—*Izvest. Akad. Nauk S.S.S.R. Otdel. Tekh. Nauk 1955,* No. 7, 137).

Corrosion-inhibiting polymeric organosilicon compositions were stabilized with certain tin compounds such as dibutyltin dilaurate (Rossiter & Currie—*U. S. 2,742,368*). An anticorrosive for wells and pipelines contained fatty quaternary ammonium halides, fatty amines, and polyglycol ethers of an ethanolamine (Cardwell & Alderman—*U. S. 2,745,809*). A hydrocarbon oil anticorrosive coating contained fatty acid ester of dextran to improve adherence (Hiler—*U. S. 2,756,156*). A similar product contained calcium soap of fish oil fatty acids, polymerized isobutylene, and microcrystalline wax to thicken the product (Cooke & De Hoff—*U. S. 2,758,981*). Another comprised mineral oil containing small amounts of oleic acid, coconut fatty acid amine salt, and petroleum sulfonate (Cantrell & Fisher—*U. S. 2,763,614*). Small amounts of fatty alcohol ester of N-hexylsuccinamic acid and alkyl amines were also added to mineral oil rust-inhibiting compositions (Messina—*U. S. 2,742,432*). The use of fatty acid trimethylene diamine salts in metal paints to inhibit corrosion of the metal and peeling of the paint was patented (Riegler & Atherton—*U. S. 2,772,174*). Other fat-derived anticorrosive compositions were a mixture of urea, inorganic nitrite, and fatty acid amine (Senkus—*U. S. 2,739,871*), a fatty amine glycolate (Gunderson—*U. S. 2,767,106*), and polyamine derivatives of fatty acids (Pfohl & Gregory—*U. S. 2,736,658*).

Patents were issued on several deep well drilling fluids or "muds" which contained soap or fat derived surface-active agents as emulsifiers (Barron—*U. S. 2,719,120*; Rowe—*U. S. 2,727,002*; Moore—*U. S. 2,747,839*; Hoeppel—*U. S. 2,754,265*; Schlack & Arnold—*Ger. 828,081, Cl. 5a*). Cadmium and barium oleates were added to drilling muds to reduce fluid loss due to filtration (Engle—*U. S. 2,759,890*).

A patented hydraulic transmission fluid comprised a major portion of lubricating oil and small amounts of alkyl phenol sulfide, fatty acid, and fatty mercapto acetic acid (Howell & Wasson—*U. S. 2,731,418*). A glycol-type pressure transmitting fluid contained soap and other materials (White & Sawyer—*U. S. 2,751,355–6*). Fatty amido compounds were added to fuel oil to inhibit the separation of sludge (Mattson & Scott—*U. S. 2,736,641*).

Offset and blocking effects are inhibited in antihalation layers consisting of dye or pigment and gelatin by incorporating a small amount of fatty acid amide (Richman & Easton—*U. S. 2,732,305*). An oil-soluble ink remover comprised a mixture of paraffin, lanolin, stearic acid, emulsifier, and water (Kawano—*Japan 7323*-'54). In telegraphic facsimile transmission with electric stylus, the blank sheet pickup was insulated with a wax composition which contained in part stearic acid (Kline & Roddin—*U. S. 2,751,310*).

Incendiary fuels, comprising hydrocarbon gels thickened with aluminum soap, were improved in stability and consistency by addition of aluminum aerogels (Goldenson & Cohen—*U. S. 2,769,697*). Other newly patented incendiary gels were gelled with aluminum iso-octanate (van Strien *et al.*—*U. S. 2,751,283–4, 2,751,350, 2,751,360–1*; Cohen—*U. S. 2,741,629*).

Aluminum soaps of certain mixtures of the hydrogenated fatty acids of fish oils or tallow and coconut oil were 3–4 times as economical in the formation of gels as conventional aluminum stearate (Mason *et al.*—*U. S. 2,758,123*). Aluminum soap prepared by adding aqueous sodium soap solution to a 2–10% excess of aqueous aluminum salt solution, while stirring, had good and uniform gelling properties (Bulloff—*U. S. 2,768,996*). The preparation of pure tristearate, tripalmitate, trimyristate, trilaurate, and trivalerate of aluminum is possible by distilling out isopropanol from a mixture of aluminum isopropoxide and excess fatty acid in benzene (Mehrotra & Pande—*J. Inorg. Nuclear Chem. 2*, 60). This has been confirmed by x-ray analysis, and some physical and chemical properties of pure aluminum tristearate were recorded (Gilmour *et al.*—*J. Chem. Soc. 1956*, 1972). Surface pressure-area curves of myristic acid on hydrochloric acid and potassium aluminum sulfate solutions were studied and interpreted with regard to the aluminum soap composition (Ekwall & Brum—*Acta Chem. Scand. 9*, 1057, 1069). The analysis of skimmed monolayers corresponded to a mixture containing one mole of aluminum with between 2–3 moles of myristate radical. Soaps of lithium, calcium, barium, aluminum, and lead were prepared and examined with the electron microscope (Kling & Mahl—*Fette-Seifen-Anstrichmittel 58*, 489). Other literature on water insoluble metal soaps pertains to uses in lubricants and as paint driers and will be cited later.

Drying Oil Products—Paints, Resins, and Plastics. The general informative communications on these subjects were written on: recent research on drying oils (von Mikusch—*Seifen-Öle-Fette-Wachse 82*, 113, 141, 169), fatty acid uses in the protective coating industry (Lang—*Paint Varnish Production 46*, No. 9, 31), the composition of Indian tung oils (Chakrabarty & Chakrabarty—*Sci. & Culture, India, 21*, 326), influence of aging on the properties of tung oil (da Fonseca & Schneiderman—*Bol. dept. quim. escola politec, Brazil, 1*, 1), evaluation of dehydrated castor oil in exterior white house paint (Patton—*Offic. Dig. Federation Paint & Varnish Prod. Clubs 27*, 627), use of *Lallemantia iberica* oil in paints and varnishes (Petit—*Rev. franc. corps gras 3*, 272), transformation of grape seed oil into a drying oil (Martinez-Moreno—*10th congr. intern ind. agr. y aliment. Madrid 1954*, 1045), methods and advantages of conjugation (Bush—*Am. Paint J. 40*, No. 46, 80; No. 48, 98; No. 50, 80; No. 51, 78; No. 52, 97; *41*, No. 1, 78), conjugation in drying oils (von Mikusch—*Paint Manuf. 25*, 386), vegetable oil polymerization (Sims—*Chemistry in Can. 8*, No. 6, 71), stability of thermal polymers to autoxidation (Aaland—*Univ. Microfilms, Ann Arbor, Mich. Publ. No. 15176*, 61 pp.), epoxidation and uses of epoxides in coatings (Swern—*Paint Varnish Prod. 46*, No. 5, 27; No. 6, 29; No. 7, 35; No. 8, 32), epoxide resins in metal finishing (Wheeler—*Trans. Inst. Metal Finishing, London 30*, 158), uses of maleic-modified oils (Heilmann—*Farbe u. Lack 61*, 564), new developments in alkyd resins (Muller—*Paint Ind. Mag. 71*, No. 3, 26), alkyds from tallow acids (Schwartz & Lutz—*Paint Varnish Prod. 45*, No. 12, 35), maleic anhydride adducts (Slansky—*Paint Manuf. 26*, 166), commercial pentaerythritol (Chatfield—*Paint, Oil & Colour J. 128*, 824), metal stearates for the paint industry (Stumpf—*Paint Manuf. 25*, 453; *26*, 117), polyvinyl acetate emulsion paint systems (Terry—*Paint Ind. Mag. 71*, No. 4, 14), emulsion diluent for oil paints (Ivanov—*Byull. Stroitel. Tekh. 13*, No. 4, 17), alkyd type exterior home paints (Lilley—*Paint Ind. Mag. 71*, No. 3, 15), and blown oils in the paint and ink industries (Lopez—*Grasas y aceites, Spain 6*, 187).

Several communications pertained to the mechanisms taking place during the polymerization of oils. A study of the reactions occurring in the autoxidation of methyl linoleate show that there is concurrent oxidation of some of the original hydroperoxides formed with all stages of oxidation of methyl linoleate (Privett & Nickell—*J. Am. Oil Chem. Soc. 33*, 156). In this work analyses of hydroperoxides oxidized to varying degrees indicated that *trans, trans* diene conjugation and isolated *trans* double bonds produced in oxidation of linoleate are related to the concurrent oxidation of accumulated hydroperoxides. Similar work by Sephton & Sutton (*Ibid.* 263) has indicated that the autoxidation of linoleate produced *cis, trans* and *trans, trans* isomers, and that there was a possibility that conjugated *cis, cis*-forms were also produced. In the catalyzed thermal polymerization of methyl eleostearate at treating temperatures below 260°, the products were mainly dimers and contained about one ring (cyclization) per molecule; after polymerization at 290° the product contained two rings per mole (Boelhouwer *et al.*—*Research, London 8*, No. 9, Suppl. 46). Another investigation of the polymerization of β-eleostearate revealed that dimer concentration goes through a maximum as polymerization temperature approaches 285° and after all triene system had disappeared (Maschka & Müller—*Monatsh 86*, 397). Several investigators polymerized linseed oil or certain highly unsaturated acids; recorded the changes in characteristics during the course of the polymerization; and submitted chemical and/or spectroscopic evidence that cyclization takes place during the process (Mehta & Sharma—*J. Am. Oil Chemists' Soc. 33*, 38; MacDonald—*Ibid.* 394; Floyd *et al.*—*Ibid.* 609; Rivett—*Ibid.* 635). Hoeve (*J. Polymer Sci. 21*, 1, 11) and Hoeve & Sutton (*J. Am. Oil Chemists' Soc. 33*, 312) reported that Florys' polycondensation theory can be applied to polymerization of oil, because during the heating interesterification occurs to a state of random distribution of fatty acids among the glycerides. This condition is required for application of the theory and equations to the polymerization. This theory which assumes that no ring formation occurs has been extended to include this effect. A study of the kinetics of a Diels-Alder-type reaction with diethylazocarboxylate and *trans, trans*-9,11-octadecadienoic acid demonstrated that: (a) the reaction is faster in polar solvents than in nonpolar solvents; (b) addition of acid catalysts to nonpolar solvents increase the rate of reaction; and (c) when compatibility can be maintained, addition of water to polar solvent systems increased the reaction rate in proportion to the amount of water added (Gast *et al.*—*J. Am. Oil Chemists' Soc. 33*, 278).

Many additives can be used to accelerate bodying or drying of oils. Hemins, particularly the iron-complexes, accelerate molecular enlargement of drying oils (Kaufmann & Hambrock—*Fette-Seifen-Anstrichmittel 58*, 520). The accelerating effects of cobalt, manganese, and lead driers on the oxidation rate of linseed oil during bodying (Uyehara—*Offic. Dig. Federation Paint & Varnish Prod. Clubs 27*, 794), and on the polymerization rate of linsed and tuna fish oils (Lopez-Morales & Doadrio—*Anales real soc. espan. fis. y quim., Madrid 51B*, 541) have been evaluated. The newly patented polymerization catalysts were lead toluate-naphthenate (Lum—*U. S. 2,734,829*), phosphoric acid saturated with gaseous boron trifluoride (McCaleb—*U. S. 2,730,520*), acetic anhydride (Grummitt—*U. S. 2,754,308*), and polyethylene wax of molecular weight 2000–4000 (Gearhart & Crowley—*U. S. 2,739,975*). Improvements in the bodying and drying of oils are also obtained by isomerization. The reagents that were used to promote this structural change were alkyl iodides (Goldblatt—*U. S. 2,744,123*), inorganic iodine compounds (Pack & Planck—*U. S. 2,760,968*), iodine (Chipault—*Ann. Rept. Hormel Inst. 1955–6*, 11), anthraquinone (Prakash *et al.*—*Paintindia 5*, No. 12, 21), mono- or dichlorourea (Kaufmann & Baltes—*Ger. 905,976, Cl. 12o*), phenyl sodamide (Tomiyama *et al.*—*Japan 438*-'55), and N-bromosuccinimide (Nanavati *et al.*—*Chemistry & Industry 1956*, 82).

Hydroxy oils, generally castor oil, were converted to drying oils by dehydroxylation. Some methods recently described for this purpose pertained to heating the castor oil with the following catalysts, respectively: sulfur dioxide (Nauroy—*Fr. 992,192*), a mixture of zinc and sodium bisulfate (Korshak & Ivanova—*Zhur. Priklad. Khim. 28,* 523), acid sodium pyrophosphate (Soc. Carpentier Lefebvre & Fils—*Fr. 988,655*), copper sulfate or tungsten trioxide (Huesa-Lopez—*Gracas y aceites, Spain, 6,* 23), and clay (Canchela & Cruz—*Philippine J. Sci. 84,* 303). Castor oil was also dehydrated by preparing estolides with the fatty acids from cottonseed oil and heating at temperatures that will split and distill off the combined cottonseed oil acids (Jordan—U. S. 2,745,854). The dehydration of castor oil was reviewed with regard to preparation of tung oil substitutes (Saboor—*Bengal Ind. Res. Board Bull. No. 113,* 9 pp.).

Several other means are used to convert oils with poor drying properties to drying oil uses. Heating herring and sardine oils with di-*tert.*-butyl peroxide increased molecular weight and viscosity without increasing unsaturation, retarded darkening upon heating, reduced fishy odor, and accelerated drying to give harder films (Tess & Dannenberg—*Ind. Eng. Chem. 48,* 339). In this work the changes effected in the oils named and linseed oil on heating with the reagent are recorded. The drying properties of calamory and linseed oils were improved by high frequency silent discharge under low hydrogen pressure (Gotoda—*J. Electrochem. Soc. Japan 23,* 641). The drying properties of tall oil fatty acids were improved by heating with zinc (Nevin—*U. S. 2,763,638;* Unilever Ltd.—*Brit. 735,697*). Other means described for upgrading oils for drying uses involved: converting the fatty acids of the oils to sugar esters (Gibbons—*U. S. 2,759,922–3,* Takeshita—*J. Japan Oil Chemists' Soc. 4,* 245), treating with fumaric acid and converting to pentaerythritol esters (Hempel & Marling—*U. S. 2,754,307*), condensing with ethylene (Block—*U. S. 2,719,164*), modifying with maleic anhydride (Doadrio & Marzol—*Anales real soc. espan. fis. y quim., Madrid 51B,* 531), and reacting partial glycerides of the oils with butyl orthotitanate (Kiselev & Ermolaeva—*Zhur. Priklad. Khim. 29,* 432). Soybean, milkweed seed, and fish oils were submitted to selective acidolysis by heating in the presence of anthraquinone with distillation of the liberated acids to yield a residue of drying oils which set to firm films (Lanson—*J. Am. Oil Chemists' Soc. 33,* 68). Heating of sulfur-olive oil foots produced some polymerized material which can be depolymerized with strong caustic (Gracian *et al.—Fette-Seifen-Anstrichmittel 58,* 353). *Ongokea klaineana* kernel oil which is composed essentially of triglycerides of a fatty acid containing one double bond and two triple bonds was converted to a drying oil by condensing with polyisocyanates (Müller—*Ger. 828,577, Cl. 22h*).

Products ranging from improved drying oil to resinous solids were made by copolymerizing fatty material with: ethylene (Takeshita—*J. Japan Oil Chemists' Soc. 5,* 11), aromatic vinyl compounds (Lowe & Butler—*U. S. 2,736,716;* Frazier—*U. S. 2,736,717;* Ehring & Raichle—*U. S. 2,734,880;* Kirsch—*U. S. 2,743,249;* Sample & Sturges—*U. S. 2,746,942;* Taat—*U. S. 2,761,850;* Bloch & Hoffman—*U. S. 2,762,712;* Dunlap & Reiff—*U. S. 2,767,151;* N. V. de Bataafsche Petrol. Maatschappij—*Dutch 77,877;* Stadelmann—*Ger. 923,391, Cl. 39c;* Gumlich *et al.—Ger. 912,150, Cl. 39c*), vinyl acetate (Schwartz *et al.—Am. Paint J. 40,* No. 3-B, 24; Ropp—*U. S. 2,727,-871-3*), aliphatic polyolefinic hydrocarbons (Block & Hoffman —*U. S. 2,762,712*), hydroxylated polybutadiene (Shotton—*U. S. 2,741,397*), dicyclopentadiene (Antykov—*Zhur. Priklad. Khim. 28,* 1215); and 2,3-dimethyl-1, 3-butadiene (Kern *et al. —Makromol. Chem. 16,* 21). Drying products were also prepared by vinylation of unsaturated fatty alcohols (Teeter *et al.—J. Am. Oil Chemists' Soc. 33,* 399).

An analysis of styrenated methyl linoleate showed that the main product was an one-to-one addition compound probably formed by a Diels-Alder mechanism (Tiong & Waterman—*J. Appl. Chem., London 6,* 197; Tiong *et al.—Anal. chim acta 14,* 228). A radiotracer study of analytical methods for styrenated oil acids and esters has indicated that solvent fractionation methods do not always work, and therefore require supplementary analysis of the separated fractions (Bobalek *et al.— Anal. Chem. 28,* 906).

Drying oil substitutes were made by polymerizing or condensing certain unsaturated hydrocarbons derived from petroleum (Ernst & Betts—*U. S. 2,719,163;* Polly & Cunningham—*U. S. 2,721,188;* Jaros *et al.—U. S. 2,728,801;* Koenecke—*U. S. 2,733,267;* Hamner—*U. S. 2,753,382;* Gleason—*U. S. 2,753,-385, 2,762,851;* Koenecke & Nelson—*U. S. 2,773,780;* Szabo & Frazier—*U. S. 2,774,780;* Badische Anilin & Soda-Fabrik A.-G. —*Brit. 744,468;* Carlsohn & Hulsmann—*Ger. 847,501, Cl. 39c;* Arocena & Riges—*Span. 212,341*). Other drying oil substitutes were made from the nongelling constituents of bituminous material (Pickell—*U. S. 2,748,011, 2,752,264*) and organic silicon compounds (Sample & Sturges—*U. S. 2,746,942,* Plueddemann & Hatcher—*U. S. 2,717,900*).

Modified alkyd resins were described in both patents and journal literature. Sunflower oil was converted to an alkyd resin by heating with terephthalic acid, and glycerol (Kogan & Kitaigorodskii—*Zhur. Priklad. Khim. 29,* 628). The segregation of polyunsaturated acids of soybean oil by urea separation methods and their conversion to alkyd resins was described (Sakurai & Fujiwara—*J. Chem. Soc. Japan, Ind. Sect. 58,* 934). A thixotropic alkyd resin composition was made from a mixture of fumaric acid, phthalic anhydride, propylene glycol, fatty acids and styrene (Lindsay & Yeoman—*U. S. 2,743,309*). Alkyd resins were modified with pentaerythritol and trimethylethane to improve water resistance (Park—*Offic. Dig. Federation Paint Varnish Production Clubs 27,* 371). Allylic alcohol and an oxirane compound were added to induce resistance of the dried films to acetone and xylene (Gregg—*U. S. 2,729,623*). To gain various characteristics, alkyds were modified with: lecithin and rosin amine (Unger—*U. S. 2,738,-337*), esters of β-keto acids and lower alcohol (Vogel & Bader —*U. S. 2,730,517*), epoxy phenolic ethers (Cody & Wollan—*U. S. 2,731,429*), allyl compounds (Cheng & Hsia—*Chemistry, Taiwan, 1955,* 125), silicone compounds (Kress—*U. S. 2,735,-825;* Miller—*U. S. 2,768,149-50*) and styrene (Lewis—*Brit. 735,764;* Daniels & Corkum—*U. S. 2,748,092;* Beavers & Urban —*U. S. 2,727,870;* Am. Cyanamid Co.—*Brit. 738,096*).

γ-Radiation moderately reduced the induction of the drying period of wet films of soybean oil alkyds, but had little effect on the physical properties of the ultimately cured film (Carrick & Sun—*Paint Varnish Prod. 46,* No. 2, 30). The pentaerythritol esters used in making oil modified alkyd resins should be low in ash content to reduce darkening or turbidity in the final resins (Müller—*Fette-Seifen-Anstrichmittel 58,* 839).

A simplified method for analysis of alkyd resins involves determination of the per cent fatty and rosin acids and the saponification value, and calculating the amount of phthalic anhydride from the results (Davidsohn—*Paint Tech. 19,* 301). The method assumes that phthalic acid is the only dibasic acid in the resin. A more completely informative analysis involved saponifying, segregating the split components, and infrared spectroscopic analysis of the fractions (Rouir & Dietz—*Industrie chim. belge 20,* Spec. No., 463). The infrared spectrum was given for all the common constituents of alkyd resins.

The epoxidation of fatty acids by hydrogen peroxide, acetic acid and a small amount of sulfuric acid was patented (Food Machinery and Chem. Corp.—*Brit. 739,609*). Various epoxide resin compounds were used with fatty oils or fatty derivatives in the preparation of varnish and plastic materials (Beacham —*U. S. 2,733,222;* Greenlee—*U. S. 2,731,444, 2,759,901, 2,760,-944*). A spectroscopic study of epoxy resin-ethylene-diamine reactions in curing of films has suggested that the long fatty acid chains in the resin impart a looser molecular structure to the cured film, which is softer in the early stages of curing (O'Neill & Cole—*J. Applied Chem. 6,* 356).

''Rilsan,'' a resin prepared from castor oil, by pyrolysis, separation of undecylenic acid, conversion of this with ammonia to 11-amino-undecanoic acid, and polymerization of this to the polyamide, has been described with regard to properties and uses (Desalme—*Rev. franc. corps gras 3,* 266). Polyamides derived from polymeric fatty acids were made for use in coatings or as adhesives (Wittcoff—*U. S. 2,728,737;* Wittcoff & Renfrew—*U. S. 2,768,090*). Phenol-formaldehyde resins were esterified with higher unsaturated fatty acids and dimerized rosin to serve as ingredients for coatings highly resistant to alkali (Floyd—*U. S. 2,730,511*). A plastic product was made from castor oil, polyhydric alcohols and a diisocyanate (Simon *et al.—U. S. 2,772,245*).

Some patented stabilizers for polyvinyl chloride resins were fat derivatives. These compounds were: partially epoxidized unsaturated fatty oils (Robitschek & Stormon—*U. S. 2,731,-431*), di-*n*-butyl 9,10-epoxyoctadecane phosphonate (Hardy & Reetz—*U. S. 2,770,610*), and certain fatty acid tin derivatives (Ramsden—*U. S. 2,744,876;* Mack—*U. S. 2,745,820*).

The fat derivatives recommended for use as plasticizers were: a chlorinated methylstearate (Murata—*Japan 613-'55*), esters of 9,10-dihydroxystearic acid with ether alcohols (Knight & Swern—*U. S. 2,729,612*), polyglycol dioleate (Yost & Fredrick—*U. S. 2,751,367–8*), a mixture of amine adduct of bentonite, silica gel and aluminum distearate (Severs & Frechtling—*U. S. 2,753,314*), carbonato nitriles of fatty acids (Riedeman—*U. S. 2,755,264*), N,N-disubstituted carbonato fatty acid amide (Riedeman—*U. S. 2,755,265*), adduct of soybean oil and dialkyl fumarate (Dazzi—*U. S. 2,757,151*), dialkyl ester of epoxidized 8,12-eicosadienedioic acid (Mika & Sullivan—*U. S. 2,764,497*), a mixture of epoxidized polyester derived from oleic acid, propylene glycol and adipic acid (Aitken *et al.—Brit. 744,831*), epoxidized mixed acetylated mono- and diglycerides (Greenspan & Gall—*J. Am. Oil Chemists' Soc. 33, 391*), magnesium and zinc stearates (Baymiller—*U. S. 2,750,348;* O'Herren—*U. S. 2,750,349*), maleic anhydride adducts of the methyl esters of fish oil fatty acids (Shigeno *et al.—J. Chem. Soc. Japan, Ind. Sect. 59*, 63), and reaction products of acrylonitrile and fumaronitrile with α- and β-eleostearates (Hoffmann *et al.—J. Am. Oil Chemists' Soc. 33*, 410). Murai *et al.* (*J. Oil Chemists' Soc., Japan 3*, 2, 300) prepared many estolides from castor oil and coconut oil acids, various glycol esters, and adducts of dibasic acids with various oils and fatty alcohols, and evaluated these for use as plasticizers for polyvinyl chloride.

A small amount of ethylene distearamide was added to solid ethylene polymer to prevent cracking under stress (Happoldt—*U. S. 2,765,293*). Fatty acid amides were added to the same material to improve resistance to blocking and improve coefficient of friction (Barker *et al.—U. S. 2,770,608;* Symonds—*U. S. 2,770,609*).

Paints, varnishes and coating materials were designed or modified to induce special characteristics. Polymeric isopropoxy titanium stearate was added to paints for wood and masonry to inhibit moisture transmission and paint blisters (La Berge—*U. S. 2,750,303, 2,750,307*). A paint made from raw isano oil and a polyamide resin was fire retardant (Allen *et al.—U. S. 2,754,217*). The drying times of various artist oil-paint colors belonging to one assortment were made equal by proper dosage with a drying inhibitor and an accelerator (Koninklijke Fabrieken Talens & Zoon N.V.—*Dutch 78,824*). The coatings that were designed to dry to an orange peel texture (Rossi—*Ital. 489,578*) or a wrinkle finish (Drummond—*U. S. 2,744,832–3;* Sharma & Aggarwal—*U. S. 2,749,247;* McBride—*U. S. 2,763,568*), in general, were viscous mixtures of the best drying oils and resins containing oil drying accelerators of very high efficiency. This wrinkling property of conjugated oils and tung oil was inhibited by heating them with 6-*tert.*-butyl-1, 3-benzodioxan (Aelony—*U. S. 2,730,451*).

A technique has been designed for observing thin lacquer films with an electron microscope (Kaufmann & Gulinsky—*Fette-Seifen-Anstrichmittel 57*, 1007). Extremely fine wrinkles, pores, colloidal oil particles, driers, waxes, and other materials are visible in photographs taken in this study. By shading the films with platinum in high vacuum, fine irregularities of the film could be detected. ''Mechanical'' spectroscopy was used to study the effects on composition, aging, radiation, and leaching with water on varnish films (Brunt—*J. Oil & Colour Chemists' Assoc. 38*, 624).

A mixture of the petroleum resin, ''Petropon 1158,'' blown linseed oil, and boron trifluoride-ether complex on mild heat treatment yields a varnish-like product which is a suitable low-cost binder for sand molds, composition board, glass-fiber twine, etc. (Kiebler & Euchner—*U. S. 2,750,298*). A tacky linseed-oil-coated patent leather was treated with isocyanate vapors to harden the coating without producing brittleness (Demme—*U. S. 2,741,566*). The gelling properties of oxidized oil intended for linoleum manufacture usage was improved by admixing certain alkoxy titanium acylates (Beacham—*U. S. 2,736,666*). Mixtures of tobacco and safflower seed oils were successfully used instead of the customary drying oils in the preparation of white and brown factices that are vulcanized by sulfur or sulfur chloride (Rao & Raghunath—*J. Sci. Ind. Res., India 14B*, 425). A floor covering was prepared from inorganic and organic filler and binder made from wool fat, rosin, waxes, polyvinyl acetate, and dibutyl phthalate (Reichert *et al.—Ger. 829,060, Cl. 39b*). A cement for cementing side seams of metal cans in place of soldering was made by polymerizing castor oil with methylene bis(4-phenylisocyanate) (Yoho—*U. S. 2,769,826*). Tall oil esters of pentaerythritol were recommended for use as linoleum cements (Dunlap—*U. S. 2,752,262*). A heat-resistant metal putty comprised a mixture of linseed oil, inorganic filler, and metal powder (S. a. r. l. Establissements Collex—*Fr. 998,927*). A caulking compound for application with an extrusion gun contained filler and castor oil-dicarboxylic acid reaction product (Castner—*U. S. 2,760,877*). Cellulose acetate-butyrate was combined with 3-methoxybutyl myristate to produce a molding plastic (Meyer & Broyles—*U. S. 2,763,562*). A patented lithographic-ink vehicle comprised the reaction product of tall oil with the resinous polyhydric alcohol resulting from the reaction of bis(4-hydroxyphenyl) 2,2-propane and an epihalohydrin (McNabb—*U. S. 2,754,277*).

Fatty Materials in Lubrication, Metal Working, and Textile Oiling. The theoretical aspects of viscosity of fatty materials were reviewed and discussed with regard to relation to oxidation, polycondensation, and importance as lubricants and lubricant additives (Teeter & Cowan—*J. Am. Oil Chemists' Soc. 33*, 163). An investigation on the oiliness of palmitic acid and the corresponding alcohol on steel surfaces has shown that oiliness sharply decreases in an oxygen-free atmosphere because in this case these polar molecules are strongly absorbed by the surfaces (Nagai *et al.—J. Chem. Soc. Japan, Ind. Sec. 58*, 874).

In a report on characteristics of aging dispersions of 25% lithium stearate in hexadecane, Vold (*J. Phys. Chem. 60*, 439) suggested that lubricant greases should be classed as flocculated dispersions, in which a dominant factor in interparticle interaction is the London-van der Waals forces. Her work also indicated how processing conditions affected the structure of the mixture. A study of the flow properties of aluminum dilaurate in toluene gels showed high viscosity at low shear rates. When a critical shear stress range was exceeded, the shear rate increased rapidly with small increases in shear stress, and at high shear rates the ratio of log-shear rate *versus* log shear stress approached a constant (Weber & Bauer—*Ibid.* 270). In dilute toluene solutions of aluminum disoaps, the dielectric loss was due almost entirely to direct-current conductivity (Nelson *et al.—J. Chem. Soc. 1956*, 3463). The stability of the ions in a solvent of such low dielectric constant was explained by the shielding effect of the hydrocarbon chains which prevents close approach of the ionic charges localized in the center of the aggregates.

New formulas and techniques were used in grease making to attain special characteristics. Greases of high drop point and high ''worked penetration'' were thickened with ''salt-soap'' complexes of calcium, barium and strontium (Morway—*U. S. 2,735,815, 2,738,329*). The ''salt-soap'' complexes are mixtures of soaps of higher fatty acids with metal salts of lower fatty acids. Outstanding high temperature properties were obtained when the salt-soap complex contained calcium and one other water-insoluble-soap forming metal (Forster & Hamer—*U. S. 2,734,030*). Greases suitable over a very wide temperature range were made from salt-soap complexes of lithium (Morway & Young—*U. S. 2,739,127*). Various combinations of soaps of calcium with strontium, barium, aluminum, and sodium were used to prepare greases of good structural stability at high temperatures (Forster—*U. S. 2,733,208*). Bleeding and hardening of magnesium soap grease were reduced by addition of lithium and sodium soaps (Forster—*U. S. 2,733,209*). A mixed lithium-strontium soap was made for lubricant usage, from acids obtained in the oxidation of petroleum (Eckert—*U. S. 2,738,327*). A calcium soap for grease making was prepared from a mixture of animal fats and by-product acids obtained in the refining of lubricating oils (Stucker & Fronczak—*U. S. 2,755,248*). Novelty in some patented grease making methods pertained to methods of heat treating and working to obtain desirable physical properties (N.V. de Bataafsche Petroleum Maatschappij—*Dutch 79,051;* Dilworth *et al.—U. S. 2,755,247;* Young *et al.—U. S. 2,755,249;* Dilworth & Puryear—*U. S. 2,755,256;* Morway & Dawson—*U. S. 2,745,810*). Lithium carbonate was reacted with fatty acids in the presence of ammonia to manufacture soaps for grease making (Boner & Breed—*U. S. 2,753,364*). Equipment has been designed for continuous blending and tempering of lithium soap and mineral oils to form lubricating greases (Baker—*U. S. 2,760,936*).

In some new greases the soap gelling agent has been in part or wholly replaced by other thickeners. The materials that were used are copolymers of styrene, maleic anhydride and partially esterified mixture of alcohols (Frank—*U. S.2,737,494*), polyamides, (Dixon—*U. S. 2,752,312*), reaction product of difatty pyrrolidium halides with bentonite (Erickson—*U. S. 2,748,143*), silicone compounds (Saigo—*Japan 8685-*'54; Morway & Witts—*U. S. 2,758,973;* Hain & Zisman—*Ger. 850,047 Cl. 23c;* King & Pattenden—*U. S. 2,731,417*), inorganic gels rendered water resistant with tin halide (Marshall & Steininger—*U. S. 2,751,349*), a combination of aerogel and organic isocyanate (Weihe & Schweitzer—*U. S. 2,739,121*), metal alginate (Morway & Bartlett—*U. S. 2,754,268*), and elastic casein fiber (Morway & Spray—*U. S. 2,734,862*).

Many additives were used in lubricating greases to induce special characteristics. Fatty substituted succinic acid and tricresyl phosphate were added to lubricants for heavy journal bearings (Pokorny—*U. S. 2,730,499*). A lithium soap grease containing some aluminum octoate and monophenylphosphate had a low viscosity at —70°F. without excessive volatility at 300°F. (Butcosk—*U. S. 2,737,473*). The stability of greases at high temperatures was improved with mixtures of fatty alcohol, and esterified dibasic acids, glycols and polyglycols (Morway *et al.*—*U. S. 2,750,341, 2,751,351*), with branched high molecular weight alcohols (Cottie—*U. S. 2,746,924*), and with normal fatty alcohols (Butcosk—*U. S. 2,769,781*). The presence of calcium petroleum sulfonate in aluminum soap greases induced a wear-inhibiting effect (Hotten—*U. S. 2,719,-826*). A method for preparing sulfonates for this purpose was patented (Bray—*U. S. 2,746,987*). The additives used in extreme pressure grease lubricants are lactic acid (Beretvas—*U. S. 2,720,491*), and a mixture of boric acid, lecithin and 2-heptyl-4-hydroxy-4-ethyl oxazoline (Williams & Scott—*U. S. 2,749,310*). Adding a nitrite to a grease composition while it is in a hot fluid condition increased the drop point (Parry & Matthews—*U. S. 2,738,329*). The newly patented corrosion inhibitor additives for greases were organic orthosilicates (Merker & Zisman—*U. S. 2,735,816*) and fatty acid amide (Nagashima & Shindo—*Japan 337*-'55).

Some of the lubricating oil additives recently patented were derived from fatty materials. Condensation products of fatty acids and diamines were added to improve heat stability (Hemmer & Jouandet—*Fr. 998,053*). Similar products plus dibasic acid were used to improve low temperature lubrication oil (Hollyday—*U. S. 2,744,071*). The materials added to lubricants to confer detergency were: high metal content sulfonic acid salts (Otto & Williams—*U. S. 2,739,124*), an ester product of dicarboxylic acid glycol and amino fatty alcohol (Smith & Lippincott—*U. S. 2,764,551*), tall oil pitch-phosphorus sulfide reaction product (Hook & Beegle—*U. S. 2,731,415*), oxidized fatty acids (Compagnie francaise raffinage—*Fr. 988,-543*). Fatty mercaptans were added to motor oils to prevent lead deposition (Hill—*U. S. 2,738,330*). A mixture of terpene-phosphorus-sulfur and phosphorus sulfide-oxygen-fatty acid reaction products inhibited sludge formation in mineral lubricant oils (Hook & Peeso—*U. S. 2,734,864, 2,734,866*). A sulfured sperm oil lubricant additive of improved color stability was obtained by sulfurizing in the presence of a salt, such as sodium carbonate, disodium phosphate, or borate salt (Bloomsburg & Shearer—*U. S. 2,753,332*). The tendency of this additive to evolve hydrogen sulfide on storage was rendered by treating it with guanidine carbonate (Waddey *et al.*—*U. S. 2,735,817*). The patented rust inhibitors for lubricating oils were a mixture of dimerized fatty acids and partial esters of alkitol anhydrides (Gottshall & Kern—*U. S. 2,767,144*) and a condensation product of phenols and fatty acids (Messina & Snead—*Ind. Eng. Chem. 48, 2001*). In using commercial sulfonates as lubricant additives, the low molecular weight material in the product should be removed to reduce corrosiveness (Muffley *et al.*—*Corrosion 12*, 411t).

An aqueous-type lubricant, particularly useful for low-speed Diesel engines operating on fuels high in sulfur, consisted of lubricant oil, glycerol monoöleate emulsifier, and a 25% solution of calcium acetate (Stillebroer & van der Minne—*U. S. 2,744,870*). A synthetic lubricant oil was a blend of C_6–C_{16} branched-chain alcohol diesters of dibasic acids, branched chain C_6–C_{16} alcohol half esters and condensates of sebacic acid and polyethylene glycol, and a primary or secondary amine (Matuszak & Wilson—*U. S. 2,743,234*). An instrument lubricant usable as low as −100°F. contained branched chain C_5–C_8 alcohol ester of dibasic acid, lithium soap, and an oxidation inhibitor (Culnane & Dilworth—*U. S. 2,721,844*).

Lubricant characteristics for drawing of sheet metal were discussed with regard to film strength, heat resistance, antiwelding, corrosive effect, application, removal, and cost (Viers—*Steel 139*, No. 2, 86; No. 3, 148; No. 4, 94). New federal specifications have been issued for sulfurized-lard oil-cutting oil base (No. C-C—*800*, 4 pp.). Many patented emulsion type compositions, designed as lubricants and coolants in metal cutting, turning, drilling and stamping, included one or more fatty substances and/or fatty derivatives in their formulas (Reamer—*U. S. 2,722,515;* Schuster & Whitenight—*U. S. 2,-739,915;* Baker & Nelson—*U. S. 2,744,070;* Waugh—*U. S. 2,-773,035–6;* N.V. bataafsche Petrol. Maatschappij—*Dutch 79,-100;* Weitenhiller & Schuth—*Ger. 889,346 Cl. 23c*). Fatty materials generally used in these are fats, oils, soaps, detergents, fatty amines and sulfured fatty oils. Forging dies heated to 500–600°F. were lubricated with a mixture of polyethylene monoöleate, polymerized fish oils, bentonite, graphite, and hemicellulose (Hodson & Foin—*U. S. 2,735,814*). Many wire drawing lubricant compositions were patented. These were: a mixture of mineral and fatty oil containing powder of metal to be extruded (Tschudnowsky—*Ger. 829,038 Cl. 23c*), and special mixtures of soap or detergent, borax, filler, and various modifying agents (Orozco—*U. S. 2,753,304;* Whitbeck—*U. S. 2,753,305;* Spring & Blum—*U. S. 2,760,931;* Carhart—*U. S. 2,736,699*). One lubricant for the same purpose contained linseed oil, graphite, carbon, saw-dust and pyrolusite (Clatot—*U. S. 2,757,138*). A lubricant for cold drawing of thorium wire comprised lacquer vehicle containing suspended molybdenum sulfide and lead or zinc oxide (Graham & Donley—*U. S. 2,736,700*). For making rock drilling lubricant, mineral oil was blended with tritolyl phosphate, sulfurized lard oil, lecithin and polyisobutylene (Bright & Hall—*U. S. 2,734,868*).

The textile lubricants described during the year were emulsions of mineral oil and water containing fat derived emulsifiers and other modifiers some of which were derived from fat. One such emulsion contained condensation product of fatty acid methanolamide and thioglycolic acid as the emulsifier and a high boiling alcohol to retard evaporation (Maeder & Albrecht—*U. S. 2,740,759*); another contained alkyl esters of castor oil acids, oxidized peanut oil, sulfonated olive oil, sulfated higher fatty alcohol, fatty amine and alkyl phosphate (Duke & Hohing—*U. S. 2,727,860*); and another mixture included partial ester of phosphoric acid with decyl alcohol, condensation product of triethanolamine and coconut oil fatty acids, triethanolamine, diamyl phenol and polyethylene oxide ester of lauric acid (Fortess & Hohing—*U. S. 2,730,498*).

Deterioration of Fatty Materials

REVIEWS. The reviews and general information communications pertaining to the deterioration of fatty materials were written on: mechanisms of fat oxidation (Koch—*Bakers' Dig. 30*, No. 2, 48), rancidity of olive oil and lard (Alcalá—*Grasas y aceites [Spain] 7*, 94), rancidity in lard (Romero—*Ibid. 6*, 30), stabilization of olive and other fats (Gutiérrez-Quijano *et al.—10th congr. intern. ind. agr. y aliment. Madrid 1954*, 553), autoxidation and antioxidants (Ramos—*Agron. Lusitana 17*, 17), volatile matters produced by autoxidation of methyl oleate, oleic acid, and *cis*-9-octadecene (Fritsch—*Univ. Microfilms (Ann Arbor, Mich.) No. 15832*, 120 pp.), spoilage of food fats and its inhibition (Franzke—*Urania, Ger., 18*, 392), the control of rancidity in milk (Herrington—*J. Dairy Sci. 39*, 1613), antioxidants (Ruys—*Rev. franc. corps gras 3*, 163; Paquot—*Parfums-cosmét-savons No. 122*, 20), spoilage of fat and antioxidants (Raeithel—*Fette-Seifen-Anstrichmittel 57*, 799), stabilization of fats, fatty oils, and oil-soluble vitamins (Bucher—*Bull. Galenica 14*, 155, 189), use of butylated hydroxyanisole to stabilize edible fats (Emanuel *et al.*—*Myasnaya Ind. S.S.S.R. 26*, No. 6, 47), butylated hydroxytoluene as an antioxidant (Tollenaar & Vos—*Fette-Seifen-Anstrichmittel 58*, 112), microbiological deterioration of margarine (Maltschewsky—*Ibid.* 331), evaluation of 232 bacterial inhibitors for effectiveness against microörganisms in metal cutting oils (Bennett—*Soap & Chem. Specialties 32*, No. 10, 47; No. 11, 46), and lipoxidase catalyzed oxidation (Lundberg—*Fette-Seifen-Anstrichmittel 58*, 329).

TESTS FOR DETERIORATION, STABILITY, AND ANTIOXIDANTS. Methods for the determination of the peroxide value of fats and oils were investigated. Franzkes' (*Z. Lebensm.-Untersuch. u.-Forsch. 103*, 108) comparisons of the iodometric methods of Lea, Taufel & Rothe, Hadorn & Jungkunz, and Sully have indicated that the method of Taufel & Rothe was most rapid and simple but gave high results. To correct the deviation one must modify the procedure to eliminate the effect of atmospheric oxygen. The results of the Sully method were most reproducible, but the method was considered too tedious. In similar work by Hadorn *et al.* (*Ibid. 104*, 316) a deviation of results by the Hadorn & Jungkunz method at high peroxide values from those of other methods was corrected by using very finely powdered potassium iodide rather than crystals. This group found that a modified Wheeler procedure was preferable to any of those named above. Two colorimetric methods for quantitatively determining organic peroxides were based on reaction, respectively, with diamino-diphenylamine and with methylene blue (Ueberreiter & Sorge—*Angew. Chem. 68*, 352).

Some suggestions were proposed for determination of stability of fats by the accelerated oxidation methods. A new constant temperature bath for the Swift's Accelerated Oxidizability Method comprised an electrically heated and thermostatically controlled solid brass block containing holes for the samples (Schroeder & Draper—*J. Am. Oil Chemists' Soc. 33*, 628). An improvement in a procedure based on measuring the amount of oxygen absorbed pertained to electrically recording oxygen uptake (Lancaster *et al.*—*Ibid.* 36). A stability procedure by Palladina & Stepanova (*Masloboino-Zhirovaya Prom. 22*, No. 4, 16) was based on exposing one gram samples on filter paper to ultraviolet light for 5, 15, and 20 minutes and determining oxidative changes after each period.

Evaluation of deterioration or quality of fatty soap stock through estimating deterioration products was studied (Burnet & Desnuelle—*Rev. franc. corps gras 3,* 325). The methods based on insolubility of oxidized compounds in petroleum ether and on determination of single oxidized components were shown to give exceedingly low results, so a new method was designed based on adsorption of oxidized components on columns of rubber swelled with ligroin and elution of oxidized products with aqueous-acetone mixtures.

Several analytical procedures pertaining to deterioration and its prevention were made on estimation of antioxidants. A colorimetric method described for butylated hydroxyanisole in fats was based on reaction with potassium ferricyanide (Krishnamurthy & Swaminathan—*Current Sci., India, 25,* 16). A scheme for determining the antioxidant present in a fat was based on steam distillation to separate butylated hydroxyanisole and butylated hydroxytoluene, determining sum of both with ferric chloride-2,2-bipyridine and the latter alone with 2,6-dichloroquinonechloroimide; extracting nordihydroguaiaretic acid and propyl gallate from a carbon tetrachloride solution of the fat with 50% ethanol and determination with ferrous sulfate buffered to an appropriate pH (Anglin *et al.—J. Agr. & Food Chem. 4,* 1018). Infrared spectrometry was also demonstrated for studying fat-antioxidant mixtures (Hall & Clark —*Food Tech. 10,* 384). This study showed that the lecithin present in an oil forms a complex with citrate. Paquot & Mercier (*Rev. franc. corps gras 3,* 333) proposed measuring the oxidation-reduction potential of stabilized oils to estimate the residual activity of the antioxidant present. The potentials for several common antioxidants were recorded.

MECHANISMS OF AUTOXIDATION. The new information on mechanisms of oxidation pertained to the course of the reactions involved and on the oxidation products that develop. Nechaev (*Myasnaya Ind. S.S.S.R. 27,* No. 3, 46) recorded induction period, peroxide value, iodine value, acidity, absorption of oxygen, and epihydrin aldehyde development during rancidification of beef, pork, and butter fat samples. These data were discussed with regard to correlation of various analytical and organoleptic characteristics and the effect of light on the relationships. Similarly Malhan & Kartha (*J. Sci. Ind. Research, India, 14B,* 673; *15B,* 326) recorded acidity and maximum peroxide values attained by various fats on incubation at 96°. The maximum peroxide value attained by oleic acid was 6–10; and the figures for other materials were: oleyl alcohol 150–60, triolein 220–30, ethyl oleate 360–70, peanut oil 178, sesame oil 134, lard 120, and ghee 160. In a study of the volatile products of autoxidized menhaden oil, Chipault (*Ann. Rept. Hormel Inst. 1955–6,* 61) also recorded the alterations in the characteristics. He tentatively identified aldehydes of two to seven carbon chain length among the volatile products formed on autoxidation.

Autoxidation of methyl oleate, oleic acid, and *cis*-9-octadecene at 80° induced the development of the following volatile decomposition products: formic, acetic, caprylic, enanthic, pelargonic and caproic acids (Fritsh & Deatherage—*J. Am. Oil Chemists' Soc. 33,* 109). In this work the mechanism of decomposition was discussed with regard to the earlier postulates of Rieche and of Walsh. In another like investigation propionaldehyde, *n*-hexanal, crotonaldehyde, 2-pentenal and 2-hexanal were also identified among the volatile products (Toyama & Suzuki—*J. Chem. Soc. Japan, Ind. Sect. 58,* 52). Uncatalyzed oxidation of oleic and elaidic acids was similar in formation of oxo acids, peroxides, ketol, dihydroxystearic acid, and cleavage products, except that the oxo acids developed from the former were less stable than those from the latter (King—*J. Chem. Soc. 1956,* 587). In this work cobalt catalyzed oxidation of oleic gave higher yields of fission products than uncatalyzed oxidation or oxidation of elaidic acid. The dihydrostearic acid isolated from noncatalyzed oleic oxidation consisted of a mixture of *threo* and *erythro* forms; whereas in catalyzed oxidation only *erythro* dihydroxystearic acid was observed. In a study of the autoxidation of *cis*-9,*cis*-12-octadecadiene *cis*-9, *trans*-12-linoleate and linolelaidate the *trans* bond gave a pronounced stabilizing effect to the linoleates (Privett —*Ann. Rept. Hormel Inst. 1955–6,* 7). This work indicated that peroxides in addition to diene-conjugated hydroperoxides are formed in autoxidation of linoleates and there was no evidence of formation of nonconjugated hydroperoxides.

Paquots' and Querolles' (*Ind. Chim. belge 20,* spec. No. 724) analyses of the oxidized acids in olive residue oil indicated the presence of Diels-Alder dimer of hydroxylinoleic acids, *cis*-9,-10-dihydroxystearic acid, and some unidentified carbonyl compounds. Naegamwala *et al.* (*Indian J. Dairy Sci. 7,* 178) reported that on bubbling air through buffalo and cow milk ghees at 90° for 100 hours the oxygen absorbed was distributed, respectively, as: peroxide 0.366, 0.555, acid 1.50, 0.85, aldehyde 0.03, 0.04, and hydroxyl oxygen 0.696, 0.786 g. per 100 g. of fat.

ACCELERATORS OF DETERIORATION. Hematin compounds which catalyzed oxidative fat rancidity, were found in nine species of fish (Brown *et al.—Com. Fisheries Rev. 18,* No. 2, 10). Nitrogenous inhibitors which combine with hematin compounds did not inhibit the catalytic effect in meats (Lew & Tappel—*Food Tech. 10,* 285).

Frying of fritter-type batters causes greater deterioration of frying fats than did frying potatoes (Bennion & Hanning—*J. Home Econ. 48,* 184). Baking powder, milk and eggs appeared to be the ingredients of the batter inducing the greatest decomposition of frying lard. In using vitamin A fortified ghee and vanaspati in cooking, greatest destruction of vitamin occurred during shallow frying, much less in deep frying and least during simmering (Hattiangdi & Kanga—*J. Sci. Ind. Res., India, 15C,* 48). The loss in vitamin A was greater with ghee than with vanaspati. Butter oil stored at −18° became pistachio-green in color due to crystallization and concentration of carotenoids in the mother liquid (Godel—*Molochnaya Prom. 17,* No. 2, 38). This was detrimental to the stability of the mother liquid. In Holland, Kruisheer & Krol (*Neth. Milk Dairy J. 9,* 173) recommended that only summer butter should be put in storage, for the winter butter is high in copper and does not store well.

Exposure to 10,000 ft.-candles of sunlight for one hour gave a 10-fold greater production of peroxides in almond oil with added chlorophyll than in pure oil (Lee—*Nature 176,* 463). In similar exposure of crude fats, those from raw vegetables accumulated peroxides more rapidly than those from corresponding blanched samples; except in the case of lima beans, the reverse was true (Lee—*Food Res. 21,* 254).

Cortisone, hydrocortisone, fluorohydrocortisone, and 11-dehydrocorticosterone accelerated the autoxidation of linoleic acid (Schuler & Meier—*Hoppe-Seylers' Z. physiol. Chem. 302,* 236).

STABILITY OF FATS. The autoxidative stability of cottonseed oil stored in the dark at 23–37° was not affected by winterization (Krishnamurthi *et al.—Bull. Central Food Technol. Res. Inst. Mysore 4,* 179). Yellow and white suet fats have about the same consistency, but the yellow fat is less stable (Fleischmann—*Fleischwirtschaft 7,* 722). Lard sealed in tin cans was very stable, but developed a little rancidity only at the surface which was in contact with the air in the can (Alcalá de la—*Grasas y aceites, Spain, 6,* 74).

Tests on improvement of stability of poultry fats through feeding of tocopherol have shown that chickens deposit more tocopherol in body fats and the fat stability was improved to a greater extent than in turkeys (Mecchi *et al.—Poultry Sci. 35,* 1238, 1246). The addition of chickpeas or sunflower-oil cakes to dairy cattle feeds, comprising hay and silage, reduces the keeping qualities of the butter produced (Glukhov & Morodvina—*Nauch.-Issledovatel. Inst. Zhivotnovodstva i Kormodobyvaniya Saratov 1953,* 90). The fat in experimental diets or rations made with glucose as a source of carbohydrates was more susceptible to autoxidation than in diets made with sucrose (Thompson & Hegsted—*J. Nutr. 60,* 361).

The presence of sesamolin (from sesame oil) in vitamin A fortified vanaspati was detrimental to the stability of the fat (Mathur *et al.—J. Indian Chem. Soc., Ind. & News, 18,* 123). It was suggested that vitamin A and sesamolin are incompatible. The stability of oil solutions of carotene to oxidation varied considerably with the oil used as a solvent (Shakin *et al.—Ukrain. Khim. Zhur. 20,* 408). Addition of 30% of wheat germ to the solution may reduce decomposition of carotene during eight months storage by about 50%. Addition of fats to dehydrated alfalfa meal markedly stabilized the carotene present (Ogden—*J. Agr. Food Chem. 4,* 428). In this respect, animal fats were more efficient than vegetable oils. The efficiency of the animal fats could be further enhanced by the presence of antioxidants (Siedler *et al.—Ibid.* 1023).

ANTIOXIDANTS. Several natural antioxidants were studied. The antioxidants of soybean and olive oils can be removed from the oils on adsorption columns and dissolved in petroleum ether, acetone, or ether; and those of soybean are also soluble in alcohol, whereas those of olive oil are only partly so (Heimann—*Fette-Seifen-Anstrichmittel 58,* 343). The solubility data developed here is intended for use in design of processes for production of antioxidants from oil press cake. A chromatographic investigation on the antioxidants of osage orange fruit has indicated the presence of at least four pigments with antioxidant activity (Schall & Quackenbush—*J. Am. Oil*

Chemists' Soc. 33, 80). The antioxidant activity for methyl linoleate of gossypetin and quercetagetin appeared to be, respectively, equal and three-fold that of propyl gallate on a weight basis (Lea & Swoboda—*Chemistry & Industry 1956,* 1426). In tests with spices on ground pork, cardamon, cassia, and cinnamon were slightly prooxidant; and allspice, cloves, sage, oregano, rosemary, thyme, mace, nutmeg, and turmeric increased the stability of the fat (Chipault *et al.*—*Food Tech. 10,* 209). In this work oregano was most effective in salad dressings. The antioxidants present in seeds become distributed throughout the young sprouts on germination of the seed (Dubouloz & Laurent—*Compt. rend. soc. biol. 150,* 216).

Steroids of estrogenic action, estrodiol, equilenin, estrone, and diethylstilbestrol, inhibit autoxidation of pure linoleic acid or that catalyzed by copper ions or cortisone (Schuler & Meier—*Naunyn-Schmeidebergs Arch. exptl. Pathol. Pharmakol. 228,* 474). In these tests progesterone, testosterone, and testosterone propionate were ineffective. The partial fatty esters of polyhydroxy compounds which are emulsifiers and detergents have a protective effect against the oxidation of vegetable oils (Gayte—*Parfumerie mod. 48,* No. 50, 68). Citric acid (Steinkamp—*Grasas y aceites, Spain, 7,* 89) and ascorbic acid (Cerutti—*Olii minerali, grassi e saponi, colori e vernici 33,* 25) were shown to be effective in inhibiting rancidity, particularly when used together with phenolic antioxidants.

Lard and edible beef fats were stabilized effectively by incorporation of phenolic antioxidants during steam rendering, but this effect was lost when the fat was steam deodorized (Sims & Hilfman—*J. Am. Oil Chemists' Soc. 33,* 381). In antioxidant tests with frozen ground pork, butylated hydroxyanisole was very effective and suitable (Neill & Page—*Food Tech. 10,* 315). Soybean flour was effective but it reduced the palatability rating of the pork. In similar tests on salting of salmon, butylated hydroxyanisole was most suitable, while ethyl protocatechuate and propyl gallate were rejected because of development of a violet tinge from iron impurities in the salt (Toyama & Saruya—*Bull. Japan Soc. Sci. Fisheries 21,* 248).

For stabilizing fats in candy making, Robinson (*Mfg. Confectioner 36,* 21) pointed out that choice of antioxidants should be on the basis of the fat used, and that 1–3% glycerol should be added to reduce hydrolysis. Other suggestions in candy making were that the nuts used should be dipped in an alcohol solution containing butylated hydroxyanisole 14, propyl gallate 6, and citric acid 3%, and the paper wrapping and package should be treated with 0.05% butylated hydroxyanisole (Stuckey—*Ibid. 34,* No. 6, 47).

In absence of copper, di- or triethanolamine and colamine inhibited autoxidation of animal fats, but when copper was present they had an accelerating effect (Kamalyan & Araksyan—*Biokhimiya 21,* 313). The antioxidant efficiency of various fat-soluble acids was very small when compared to the classical polyphenolic antioxidants (Paquot & Galletand—*Fette-Seifen-Anstrichmittel 57,* 1003).

Dugan & Kraybill (*J. Am. Oil Chemists' Soc. 33,* 527) studied the classical antioxidants from the standpoint of preserving the fats and the "carry-through" of this effect to crackers, pastry, and potato chips. Stability in pure fats did not correlate with stability in baked or fried products. A combination of tocopherol with butylated hydroxyanisole provided the best carry-through stability, but the tocopherol should not exceed 0.05% because lard and foods become off-flavored. Tocopherol in lards stabilized with several common antioxidants had a negative synergistic effect as measured by accelerated stability methods. A study of common antioxidants by Tollenaar & Vos (*Fette-Seifen-Anstrichmittel 58,* 112) has indicated that a combination of butylated hydroxytoluene with dodecyl gallate was most suitable for cake mixes, dodecyl gallate for powdered milk, and either butylated hydroxyanisole or butylated hydroxytoluene for lard.

Among hydroxyhydroquinone derivatives, the introduction of the *tert*-butyl group in 4-methoxyphenol increased the antioxidant potency for lard by a factor of four (Thompson & Symon—*J. Am. Oil Chemists' Soc. 33,* 414). Such increased potency was not approached by butylating any other oxyphenols. Introduction of a *tert.*-butyl group ortho to the hydroxyl group increased the antioxidant activity of 2,2-dimethyl-5-hydroxycoumaran for lard (Gleim & Chenicek—*J. Am. Oil Chemists' Soc. 33,* 322). Among 11 hydroxychromones and hydroxychromans prepared by Kawai *et al.* (*J. Pharm. Soc., Japan, 75,* 275) only 6-hydroxy-2,3-dimethylchroman and 7,8-dihydroxy-2-methylchroman were as efficient in fish oils as nordihydroguaiaretic acid. Among 18 ω-(3,4-dihydroxyphenyl)-alkanoic esters synthesized by Tamura *et al.* (*J. Agr. Chem. Soc., Japan, 27,* 318) about a third of them were about as active as the phenolic antioxidants in common use.

Schlenk *et al.* (*J. Am. Chem. Soc. 77,* 3587) have demonstrated that resistance to autoxidation can be induced in linoleates, linolenates, and vitamin A palmitate by conversion to adducts of α-dextrin, β-dextrin, and desoxycholic acid.

Patents have been issued on the following stabilizers for fats and oils: trisubstituted monohydroxyphenols (Kennerly & Hook—*U. S. 2,739,122*); the same with 2,2-alkylidenebis(4,6-disubstituted phenols) as synergists (Kennerly & Christopher—*U. S. 2,739,123*); 2,2-methylenebis(4,6-dialkylphenol) for packages and wrappers (Pullman & Porter—*U. S. 2,758,032*); a mixture of butylated hydroxyanisole, propyl gallate and citric acid in reaction product of propylene glycol and glyceride as a solvent carrier (Bentz—*U. S. 2,772,243*); 2,4,5-trihydroxybenzoic acid (Bell *et al.*—*U. S. 2,739,066*); various derivatives of trihydroxybenzene (Bell *et al.*—*U. S. 2,759,828*); 2,2-methylenebis(*tert.*-butylhydroquinone) plus a synergist (Young & McCulley—*U. S. 2,763,672*); 2,2-dimethyl-5-hydroxy-x-(1-propenyl)coumaran (Bell *et al.*—*U. S. 2,725,391*); 3,4-dihydroxyphenylpropenone derivatives (Bell *et al.*—*U. S. 2,728,-784*); the hydrochloride of ethylenediamine tetraacetic acid (Kuhrt—*U. S. 2,732,386*); acyl-*p*-aminoresorcinols (Young *et al*—*U. S. 2,730,500*); treatment (of corn oil) with acetic anhydride and a trace of sulfuric acid (Gerin—*Fr. 987,964*); a solution comprising fatty monoglyceride, citrate, propyl gallate and glycerol (Hall—*U. S. 2,758,931*); a solution of lecithin, an organic acid or phosphoric acid, and gallic acid ester in oil (Griffith—*U. S. 2,768,084*); a mixture of monoglyceride citrate, propyl gallate and water (Hall—*U. S. 2,772,170*); aromatic acids and lactones such as sinapic, ferulic, and *o*-coumaric acids (Heikel—*Czech. 83,473*); a mixture of octadecylamine, palmitic acid amide, and glycerol monostearate as a stabilizer and carrier for vitamin A (Hoffmann-La Roche & Co.—*Swiss 306,623*); alkyl-substituted catechols (Jones & Preston—*Brit. 731,067*); 4-methyl- or 4-ethylcatechol (Cowie & Jones—*Brit. 738,735*); certain new diarylmethanes (Lambert & Williams—*U. S. 2,732,407, Brit. 749,450*); 2-*tert.*- and 3-*tert.*-butyl-4-hydroxyanisole in the ratio 1:9 to 9:1 (Kraybill—*U. S. 2,746,870*); an emulsified mixture of microcrystalline wax and 2,6-di-*tert.*-butyl-4-methylphenol (Sullivan—*U. S. 2,717,880*) certain alkyl phenol derivatives (Sumiki & Tamura—*Japan 8521-'54*); combinations of polyphenolic antioxidants and citric, phosphoric, or aconitic acid (Mattil & Sims—*U. S. 2,759,829*); special mixtures of *tert.*-butyl hydroxyanisole, propyl gallate, citric acid, and ascorbic acid (Robertson—*U. S. 2,741,563*); an osage orange extract (Clopton—*U. S. 2,752,-314*); purpurogallin compounds (Thompson—*U. S. 2,770,545*); tropolone compounds (Thompson—*U. S. 2,770,546*); a combination of 2-alkyl-4-alkoxyphenol inhibitor and an alkylene polyamine (Chenicek & Rosenwald—*U. S. 2,738,281*), and α-conidendrol, β-conidendrol, or norconidendrol (Bickford *et al.*—*U. S. 2,729,671*). Lard oil and oleo oil were stabilized by selective hydrogenation of the polyunsaturated constituents and removing solid constituents by crystallization from acetone (Ault & Morris—*U. S. 2,729,659*).

OTHER TYPES OF FAT DETERIORATION. Three communications pertained to changes occurring in fat as the result of high energy radiation. Chipault & Privett (*Ann. Rept. Hormel Inst. 1955–6,* 22) recorded that under such conditions: peroxides and carbonyl compounds increase more on multiple low doses than an equivalent single large dose; that the odor developed is the same as that of ozonized fats; that methyl linoleate gives rise to solid polymers, and with sodium linoleate and oleate only soluble polymers all containing *trans* bonds; and that methyl linoleate-urea inclusion compounds give polymers which show infrared spectra characteristic of secondary amides. Dugan & Landis (*J. Am. Oil Chemists' Soc. 33,* 152) reported that irradiation with Co^{60} produced peroxides and unsaturated ketones. Tests by Lang & Proctor (*J. Am. Oil Chemists' Soc. 33,* 237) showed that irradiation of refined vegetable oils by high-energy cathode rays yielded about 0.2 moles of monocarbonyl compounds per gram per 10^6 rep. for doses up to 10^7 rep. Some of the products were themselves sensitive to the radiations, and the net yield was dependent upon a function of the concentrations and the reactivities of the precursors and the end-products. A destruction of carotenoid compounds by gamma-radiation was attributed to secondary reactions with the free radicals and the peroxides formed by irradiation (Lukton & Mackinney—*Food Tech. 10,* 630).

In the development of rancidity of flour lipides by air oxidation or by chlorine dioxide overtreatment of flour, the palatability of the flour is affected, but there is no demonstrable alteration in the nutritional value of the flour protein (Frazer *et al.*—*J. Sci. Food & Agr. 7*, 375). Vitamin E is destroyed in this process, but this was not considered to be of a serious nutritional significance for flour provides only a small percentage of our needs for this factor.

Monoglycerides from super glycerinated fats were purified of flavor reverting materials by treatment with short chain ketones, cooled until two phases formed, one of which contained reverting material, the other nonreverting monoglycerides (Young & Black—*U. S. 2,740,799*). In an analysis of the odorous flavor-reverting materials distilled from peanut oil, hexanal, several long chain normal hydrocarbons, some hydrocarbons with terminal dimethyl groupings, and sitosterol were identified (Letort & Sorba—*Bull. soc. chim. France 1956*, 69). A coconut-like off-flavor of milk fat, dried whole milk, evaporated milk, and dried cream was attributed to the presence of the lactone of 5-hydroxydecanoic acid (Keeney & Patton—*J. Dairy Sci. 39*, 1104, 1114).

Maltschewsky (*Fette-Seifen-Anstrichmittel 58*, 331, 336) reviewed and recorded new experimental data on the microbiological spoilage of margarine. Two types of margarines were stored at +20, +15, +5, —5, and —25°, respectively and the amount and types of bacteria developed in the samples and the acidity through 90 days' storage were recorded.

Physical Properties of Aceto- and Butyro-Oleins, Mono-Olein, and Diolein[1]

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GLYCERIDES CONTAINING both long- and very short-chain fatty acids have been shown to exhibit unusual properties (10, 11, 13, 19), which are of potential value in a number of practical applications (3, 9, 16). The saturated glycerides like 1,2-diaceto-3-stearin and 1-aceto-3-palmitin possess the unique property of normally solidifying to a soft, waxy polymorphic form, the alpha form, which is quite stable for these compounds. Limited experiments with aceto-oleins (10) have indicated that these glycerides also solidify in a waxy polymorphic form though these modifications generally occur at temperatures far below 0°C. Such polymorphic modifications together with other physical properties are of interest because the unsaturated glycerides are potentially useful in applications requiring low-melting oils having good resistance to oxidation, polymerization, and deterioration.

Practically no data have been published on the physical properties of the aceto- and butyro-oleins. Data are meager even for 1-mono-olein and 1,3-diolein, glycerides whose characteristics should prove useful in correlating the characteristics of the aceto- and butyro-oleins. Carter and Malkin (5) have investigated the polymorphism of 1-mono-olein and have reported the existence of four forms including a vitreous form. The expansibility and melting dilation for the highest melting form and the expansibility in the liquid state have been determined for 1-mono-olein (18). The polymorphism of 1,3-diolein has been investigated by Carter and Malkin (5), who found two polymorphic forms, and by Daubert and Lutton (8), who found one polymorphic form.

In the present investigation physical measurements were made on the following six compounds: 1-aceto-3-olein, 1,2-diaceto-3-olein, 1-butyro-3-olein, 1,2-dibutyro-3-olein, 1-mono-olein, and 1,3-diolein. Refractive indices, densities, melting points, points of transition from one polymorphic form to another, expansibilities in the solid and liquid states, and melting dilations or volume changes accompanying transformations were measured or calculated. For 1-aceto-3-olein and 1-butyro-3-olein infrared spectra, which have heretofore not been reported, were obtained.

Experimental

Materials. The 1-mono-olein used in the measurements and in the preparation of the aceto- and butyro-oleins was prepared as described in a previous publication (10). Purified methyl oleate derived from pecan oil was interesterified with glycerol, the mixed glycerides were fractionated by molecular distillation, and the mono-olein fraction was further purified by crystallization from acetone. Purity of the final product was 98.6%, as analyzed by the periodic acid method of Handschumaker and Linteris (12).

The 1,3-diolein was prepared by repeatedly crystallizing from acetone the diolein fraction obtained as a by-product in the purification of the 1-mono-olein by molecular distillation.

The 1-aceto-3-olein, 1,2-diaceto-3-olein, 1-butyro-3-olein, and 1,2-dibutyro-3-olein were prepared by direct esterification of 1-mono-olein with either acetyl or butyryl chlorides, using a procedure essentially like that described by Malkin *et al.* (15). Briefly the monoglyceride and the required quantity of acid chloride, each in chloroform solution, were mixed and allowed to react at room temperature for two days. For the preparation of the diglycerides the mole ratio of acid chloride to monoglyceride was slightly less than 1:1 while for the preparation of the triglycerides this ratio was slightly greater than 2:1. After completion of the reaction the mixture was taken up in diethyl ether and washed successively with a dilute solution of hydrochloric acid, a dilute solution of sodium hydroxide, and water. The triglycerides were further purified by several crystallizations from acetone at low temperatures. The diglycerides were further purified by first removing unreacted monoglyceride and then crystallizing the diglycerides from hexane, a procedure which will be described more fully in a subsequent article.

As a check on purity all of the compounds were analyzed for monoglyceride content (12) and hydroxyl value. The latter analysis was made according to the procedure of West *et al.* (20) except that the weight ratio of the acetic anhydride to pyridine employed was 1:4.

Analytical data for the various products are recorded in Table I. Comparison of the data for monoglyceride contents and hydroxyl values reveals small discrepancies, which are believed to have no signifi-

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